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# Photostability of CdSe Quantum Dots Functionalized with Aromatic Dithiocarbamate Ligands\_2013

Organic ligands are widely used to enhance the ability of CdSe quantum dots (QDs) to resist photodegradation processes such as photo-oxidation. Because long alkyl chains may adversely affect the performance of QD devices that require fast and efficient charge transfer, shorter aromatic ligands are of increasing interest. In this work, we characterize the formation of phenyl dithiocarbamate (DTC) adducts on CdSe surfaces and the relative effectiveness of different para-substituted phenyl dithiocarbamates to enhance the aqueous photostability of CdSe QDs on TiO2. Optical absorption and photoluminescence measurements show that phenyl DTC ligands can be highly effective at reducing QD photocorrosion in water, and that ligands bearing electron-donating substituents are the most effective. A comparison of the QD photostability resulting from use of ligands bearing DTC versus thiol surface-binding groups shows that the DTC group provides greater QD photostability. Density functional calculations with natural bond order analysis show that the effectiveness of substituted phenyl DTC results from the ability of these ligands to remove positive charge away from the CdSe and to delocalize positive charge on the ligand.

# Postsynthesis Phase Transformation for CsPbBr3/Rb4PbBr6 Core/Shell Nanocrystals with Exceptional Photostability\_2018

Lead halide perovskite nanocrystals (NCs) as promising optoelectronic materials are intensively researched. However, instability is one of the biggest challenges needed to overcome before fulfill their practical applications. To improve their stability, we present a postsynthetic controlled phase transformation of CsPbBr3 toward CsPbBr3/Rb4PbBr6 core/shell structure triggered by rubidium oleate treatment. The resulting core/shell NCs show exceptional photostability both in solution and on-chip. The solution of CsPbBr3/Rb4PbBr6 NCs can remain over 90% of the initial emission photoluminescence quantum yields after 42 h of intense light-emitting diodes illumination (450 nm, 175 mW/cm2), which is even better than the conventional CdSe/CdS quantum dots whose emission drop to 50% after 18 h under the same condition. We believe that the exceptional photostability should be resulted from the protection of the robust Rb4PbBr6 shell on CsPbBr3 NCs.

# Enhancing Photostability of Perovskite Solar Cells by Eu(TTA)2(Phen)MAA Interfacial Modification\_2019

Organic–inorganic lead halide perovskite solar cells (PSCs) exhibit spectacular changes in the photovoltaic area, but they still face the challenges of full spectral utilization and photostability under continuous light irradiation. The ultraviolet (UV) part in sunlight could induce oxygen vacancy in the mesoporous TiO2 (m-TiO2) layer, resulting in the degradation of perovskite photoactive films and the rapidly decreased device performance. In this work, we demonstrate that an effective luminescent downconversion material, Eu(TTA)2(Phen)MAA (ETPM), can be used as an interfacial modifier between the m-TiO2 layer and the perovskite photoactive layer to improve the power conversion efficiency (PCE) from 17.00 to 19.07%. The improved device performance can be ascribed to the effective utilization of incident UV light and reduced carrier recombination. Meanwhile, the conversion of the UV light by ETPM could inhibit the stability loss of the device under irradiation. As a result, the modified PSCs can maintain 86% of their initial value under continuous light soaking for 100 h, higher than that of 40% for the control device. This work indicates that the introduction of the luminescent downconversion material ETPM can successfully improve the PCE and photostability of PSCs.

# Simultaneous Enhancements of UV-Shielding Properties and Photostability of Poly(vinyl alcohol) via Incorporation of Sepia Eumelanin\_2016

Sepia eumelanin (SE), a biomacromolecule, was developed to prepare the excellent UV-shielding polymer material with better photostability. UV–vis transmittance spectra showed that poly(vinyl alcohol) PVA/SE film blocked most ultraviolet light below 300 nm even with a low concentration of SE (0.5 wt %), which still kept its high transparency in the visible spectrum. Rhodamine B photodegradation measurement further confirmed the excellent UV-shielding properties of PVA/SE film. FTIR indicated that the carbonyl absorption bands resulting from phtodegradation for PVA/SE film did not change after UV exposure for 2700 h. The tensile properties of neat PVA were deceased intensely after UV irradiation; however, those of PVA/SE film were reduced a little. Moreover, AFM indicated that the surface roughness of PVA/SE film was much lower than that of a neat PVA one. It could be concluded that SE reduced the PVA degradation rate dramatically, revealing enhanced photostability of PVA/SE film. The mechanism for outstanding UV-shielding properties and photostability of PVA/SE film was illuminated, based on the formation of charge transfer complexes (CTCs) between SE and PVA, photothermal conversion, and the well-known radical scavenging capabilities of SE.

# Photostability of Rebaudioside A and Stevioside in Beverages\_2008

The Coca-Cola Company and Cargill, Inc. have initiated the development and commercialization of the Stevia rebaudiana (Bertoni) derived sweetener rebaudioside A. Efforts were focused on high purity rebaudioside A (>97% by HPLC), commonly known as rebiana. In the course of the development program, extensive stability studies were carried out on rebiana, all supporting good stability for use in all food and beverage applications, including conditions where rebiana-sweetened beverages were exposed to light. Our findings on rebiana light stability refute those of an earlier study that suggested rebaudioside A to be unstable to sunlight exposure, while the structurally homologous stevioside is stable. We replicated the earlier study and found no significant photodegradation for either rebaudioside A or stevioside.

# Photostability of Phosphonate-Derivatized, RuII Polypyridyl Complexes on Metal Oxide Surfaces\_2012

The photostability of [RuII(bpy)2(4,4′-(PO3H2)2bpy)]Cl2 (bpy = 4,4′-bipyridine) on nanocrystalline TiO2 and ZrO2 films was investigated using a standard measurement protocol. Stability was evaluated by monitoring visible light absorbance spectral changes, in real time, during 455 nm photolysis (30 nm fwhm, 475 mW/cm2) in a variety of conditions relevant to dye-sensitized solar cells and dye-sensitized photoelectrosynthesis cells. Desorption (kdes) and photochemical (kchem) processes were observed and found to be dependent upon solvent, anion, semiconductor, and presence of oxygen. Both processes are affected by oxygen with kdes and kphoto noticeably smaller in argon saturated solution. Desorption was strongly solvent and pH dependent with desorption rates increasing in the order: methanol (MeOH) ≈ acetonitrile (MeCN) < propylene carbonate (PC) < pH 1 ≪ pH 7. Photochemistry occurred in MeOH and PC but not in aqueous, 0.1 M HClO4 and MeCN. The anion and solvent dependence of kphoto strongly suggests the photoreaction involves ligand substitution initiated by population of metal centered d-d states. The relative stability of −PO3H2- versus −COOH-substituted [RuII(bpy)3]2+ was also quantitatively established.

# C60-Decorated CdS/TiO2 Mesoporous Architectures with Enhanced Photostability and Photocatalytic Activity for H2 Evolution\_2015

Fullerene (C60) enhanced mesoporous CdS/TiO2 architectures were fabricated by an evaporation induced self-assembly route together with an ion-exchanged method. C60 clusters were incorporated into the pore wall of mesoporous CdS/TiO2 with the formation of C60 enhanced CdS/TiO2 hybrid architectures, for achieving the enhanced photostability and photocatalytic activity in H2 evolution under visible-light irradiation. Such greatly enhanced photocatalytic performance and photostability could be due to the strong combination and heterojunctions between C60 and CdS/TiO2. The as-formed C60 cluster protection layers in the CdS/TiO2 framework not only improve the light absorption capability, but also greatly accelerated the photogenerated electron transfer to C60 clusters for H2 evolution.

# In Search for the Best Environment for Single Molecule Studies: Photostability of Single Terrylenediimide Molecules in Various Polymer Matrices\_2015

Photobleaching is the main limiting factor in single molecule studies by optical techniques. We investigated the dependence of photostability of terrylene diimide (TDI) derivative on its environment using confocal fluorescence microscopy. Seven different polymers were tested. Depending on the matrix, photobleaching quantum yields vary by 2 orders of magnitude. Their values correlate with parameters characterizing oxygen mobility in polymers: diffusion coefficient and permeability. Poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) exhibit the lowest photodestruction quantum yields. Additional enhancement of photostability can be achieved by aging of PVC or by flushing the sample with nitrogen, which confirms the involvement of oxygen in photodestruction. Different character of the time traces of the intensity of emission from single TDI molecules is observed for different polymer matrices, ranging from intense blinking in the least stable polycarbonate, to practically no blinking in the most stable PVC. These results suggest a photodegradation mechanism involving self-sensitized photooxidation in oxygen complexes of TDI.

# Enhanced Performance and Photostability of Perovskite Solar Cells by Introduction of Fluorescent Carbon Dots\_2017

Perovskite solar cells (PSCs) with high efficiency have recently received tremendous attention, but the stability under light irradiation, namely, photostability, of PSCs still represents a major obstacle that must be overcome before their practical applications can be used. The degeneration of perovskite under ultraviolet irradiation from sunlight is a major impacting factor. To solve this problem, in this work we introduce fluorescent carbon dots (CDs), which could effectively convert ultraviolet to blue light in the mesoporous TiO2 (m-TiO2) layer of the traditional PSCs. As a result, CD-based devices exhibit an improved power conversion efficiency (PCE) of 16.4% on average compared to 14.6% for bare devices, and the light stability of CD-based devices is highly enhanced. These devices can maintain nearly 70% of the initial efficiency after 12 h of full sunlight illumination, while the bare devices maintain only 20% of the initial efficiency. This work indicates that fluorescent down conversion based on CDs is a novel and effective approach to improve the performance and photostability of PSCs.

# Photostability of Fullerene and Non-Fullerene Polymer Solar Cells: The Role of the Acceptor\_2019

Recently, the advent of non-fullerene acceptors (NFAs) made it possible for organic solar cells (OSCs) to break the 10% efficiency barrier hardly attained by fullerene acceptors (FAs). In the past five years alone, more than hundreds of NFAs with applications in organic photovoltaics (OPVs) have been synthesized, enabling a notable current record efficiency of above 15%. Hence, there is a shift in interest toward the use of NFAs in OPVs. However, there has been little work on the stability of these new materials in devices. More importantly, there is very little comparative work on the photostability of FA versus NFA solar cells to ascertain the pros and cons of the two systems. Here, we show the photostability of solar cells based on two workhorse acceptors, in both conventional and inverted structures, namely, ITIC (as NFA) and [70]PCBM (as FA), blended with either PBDB-T or PTB7-Th polymer. We found that, irrespective of the polymer, the cell structure, or the initial efficiency, the [70]PCBM devices are more photostable than the ITIC ones. This observation, however, opposes the assumption that NFA solar cells are more photochemically stable. These findings suggest that complementary absorption should not take precedence in the design rules for the synthesis of new molecules and there is still work left to be done to achieve stable and efficient OSCs.

# Enzymatic Oxygen Scavenging for Photostability without pH Drop in Single-Molecule Experiments\_2012

Over the past years, bottom-up bionanotechnology has been developed as a promising tool for future technological applications. Many of these biomolecule-based assemblies are characterized using various single-molecule techniques that require strict anaerobic conditions. The most common oxygen scavengers for single-molecule experiments are glucose oxidase and catalase (GOC) or protocatechuate dioxygenase (PCD). One of the pitfalls of these systems, however, is the production of carboxylic acids. These acids can result in a significant pH drop over the course of experiments and must thus be compensated by an increased buffer strength. Here, we present pyranose oxidase and catalase (POC) as a novel enzymatic system to perform single-molecule experiments in pH-stable conditions at arbitrary buffer strength. We show that POC keeps the pH stable over hours, while GOC and PCD cause an increasing acidity of the buffer system. We further verify in single-molecule fluorescence experiments that POC performs as good as the common oxygen-scavenging systems, but offers long-term pH stability and more freedom in buffer conditions. This enhanced stability allows the observation of bionanotechnological assemblies in aqueous environments under well-defined conditions for an extended time.

# Photostability of Abamectin/Zein Microspheres\_1997

Abamectin, a natural product pesticide that degrades rapidly in air and sunlight, has been encapsulated with the protein zein. The result was a mineral oil suspension that included a photostabilized abamectin. After exposure to simulated sunlight, the microsphere suspension provided a several-fold increase in recoverable abamectin residue. The enhanced photostability of the microspheres is due to retarded reaction between oxygen and the diene chromophore of abamectin, in the presence of light. The zein could function as a quencher of singlet oxygen and/or a physical oxygen barrier.  
Keywords: Abamectin; photostability; zein; encapsulation

# Co-intercalation of Acid Red 337 and a UV Absorbent into Layered Double Hydroxides: Enhancement of Photostability\_2014

Organic–inorganic hybrid pigments with enhanced thermo- and photostability have been prepared by co-intercalating C.I. Acid Red 337 (AR337) and a UV absorbent (BP-4) into the interlayer of ZnAl layered double hydroxides through a coprecipitation method. The obtained compounds were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric–differential thermogravimetric–differential thermal analysis, UV–visible spectroscopy, and the International Commission on Illumination (CIE) 1976 L\*a\*b\* color scales. The results show the successful co-intercalation of AR337 and BP-4 into the interlayer region of layered double hydroxides (LDHs) and reveal the presence of host–guest interactions between LDH host layers and guest anions of AR337 and BP-4 and guest–guest interactions between AR337 and BP-4. The intercalation can improve the thermostability of AR337 due to the protection of LDH layers. Moreover, the co-intercalation of AR337 and BP-4 not only markedly enhances the photostability of AR337 but also significantly influences the color of the hybrid pigment.

# Constructing High-Efficiency D–A−π–A-Featured Solar Cell Sensitizers: a Promising Building Block of 2,3-Diphenylquinoxaline for Antiaggregation and Photostability\_2013

Controlling the sensitizer morphology on a nanocrystalline TiO2 surface is beneficial to facilitating electron injection and suppressing charge recombination. Given that the grafted alkyl chain on a π-bridge thiophene segment for preventing π aggregation can deteriorate its intrinsic photostability, we incorporate a promising building block of 2,3-diphenylquinoxaline as the additional acceptor to construct a novel D–A−π–A-featured dye IQ4, which exhibits several characteristics: (i) efficiently decreasing the molecular HOMO–LUMO energy gap by extending its absorption bands; (ii) showing a moderate electron-withdrawing capability for an ideal balance in both promising photocurrent and photovoltage; (iii) endowing an ideal morphology control with strong capability of restraining the intermolecular aggregation and facilitating the formation of a compact sensitizer layer via two twisted phenyl groups grafted onto the quinoxaline unit. The coadsorbent-free dye-sensitized solar cell (DSSC) based on dye IQ4 exhibits very promising conversion efficiency as high as 9.24 ± 0.05%, with a short-circuit current density (Jsc) of 17.55 mA cm–2, an open-circuit voltage (Voc) of 0.74 V, and a fill factor (FF) of 0.71 under AM 1.5 illumination (100 mW cm–2). IQ4-based DSSC devices with an ionic liquid electrolyte can keep constant performance during a 1000 h aging test under 1 sun at 60 °C. Because of spatial restriction, the two phenyl groups grafted onto the additional electron-withdrawing quinoxaline are demonstrated as efficient building blocks, not only improving its photostability and thermal stability but also allowing it to be a successful antiaggregation functional unit. As a consequence, the incorporated 2,3-diphenylquinoxaline unit can realize a facile structural modification for constructing organic coadsorbent-free D–A−π–A-featured sensitizers, thus paving a way to replace the common, stability-deleterious grafted alkyl chain on the thienyl bridge.

# Antioxidant Vitamin E/Cyclodextrin Inclusion Complex Electrospun Nanofibers: Enhanced Water Solubility, Prolonged Shelf Life, and Photostability of Vitamin E\_2017

Here, we demonstrated the electrospinning of polymer-free nanofibrous webs from inclusion complex (IC) between hydroxypropyl-β-cyclodextrin (HPβCD) and Vitamin E (Vitamin E/HPβCD-IC NF). The inclusion complexation between HPβCD and Vitamin E was prepared by using two different molar ratios (Vitamin E/HPβCD; 1:2 and 1:1), which correspond to theoretical value of ∼13% (w/w) and 26% (w/w) loading of Vitamin E in the nanofiber (NF) matrix. After electrospinning and storage, a very high loading of Vitamin E (up to ∼11% w/w, with respect to fiber matrix) was preserved in Vitamin E/HPβCD-IC NF. Because of the cyclodextrin inclusion complexation, only a minimal weight loss (only ∼2% w/w) was observed. While pure Vitamin E is insoluble in water, Vitamin E/HPβCD-IC NF web has displayed fast-dissolving behavior. Because of the greatly enhanced water-solubility of Vitamin E, Vitamin E/HPβCD-IC NF web has shown effective antioxidant activity. Additionally, Vitamin E/HPβCD-IC NF web has provided enhanced photostability for the sensitive Vitamin E by the inclusion complexation in which Vitamin E/HPβCD-IC NF still kept its antioxidant activity even after exposure to UV-light. Moreover, a 3 year-old Vitamin E/HPβCD-IC NF sample has shown very similar antioxidant efficiency when compared with freshly prepared Vitamin E/HPβCD-IC NF indicating that long-term stability was achieved for Vitamin E in the CD–IC fiber matrix. In brief, our results suggested that polymer-free electrospun Vitamin E/HPβCD-IC nanofibrous webs could have potential applications in food, pharmaceuticals, and healthcare thanks to its efficient antioxidant activity along with enhanced water-solubility, prolonged shelf life, and high photostability of Vitamin E.

# Improving the Photostability of Semiconducting Polymer Dots Using Buffers\_2018

The photostability of fluorescent probes is critical in biological imaging, especially for long-term observational analyses. Here, we describe a simple and universal method to improve the photostability of semiconducting polymer dots (Pdots) and other fluorescent probes by using buffers. Using Pdots as a model system, we found that HEPES or MES buffer can improve the photostability of Pdots by a factor of 20. Through a systematic study, we show that Pdot photobleaching is dominated by photoinduced radicals which can be quenched by the piperazine or morpholine structures of these buffers, which act as radical scavengers. For conditions where choice of buffer is limited, we designed fluorescent polymers conjugated with radical scavengers to improve Pdot photostability. We then demonstrate a practical application in which HEPES buffer is used to improve the photostability of Pdots during cell imaging.

# Excellent Photostability of Phosphorescent Nanoparticles and Their Application as a Color Converter in Light Emitting Diodes\_2010

The phosphorescent Ir(III) complexes were modified by allylation and consecutive hydrosilylation, and covalently incorporated into the silica nanoparticles by hydrolysis and condensation reaction with TEOS. These nanoparticles showed an excellent photochemical and thermal stability, and a very high luminescent efficiency due to the blocking of O2 quenching and suppression of energy transfer through the amorphous silica solid solution. The limited mobility of complexes in the silica matrix also resulted in a decrease in the vibration relaxation and restrained the nonradiative decay. It is expected that these photostable and very efficient phosphorescent nanoparticles can be used in various fields ranging from nanobiotechnology to nanoengineering materials, where long-term stability with the high luminescent efficiency is required. As an example of the use of excellent photostability, a preliminary test result in which they are used as a color converter in a light emitting diode (LED) is also discussed.

# Low-Temperature Solution-Processed ZnSe Electron Transport Layer for Efficient Planar Perovskite Solar Cells with Negligible Hysteresis and Improved Photostability\_2018

For a typical perovskite solar cell (PKSC), the electron transport layer (ETL) has a great effect on device performance and stability. Herein, we manifest that low-temperature solution-processed ZnSe can be used as a potential ETL for PKSCs. Our optimized device with ZnSe ETL has achieved a high power conversion efficiency (PCE) of 17.78% with negligible hysteresis, compared with the TiO2 based cell (13.76%). This enhanced photovoltaic performance is attributed to the suitable band alignment, high electron mobility, and reduced charge accumulation at the interface of ETL/perovskite. Encouraging results were obtained when the thin layer of ZnSe cooperated with TiO2. It shows that the device based on the TiO2/ZnSe ETL with cascade conduction band level can effectively reduce the interfacial charge recombination and promote carrier transfer with the champion PCE of 18.57%. In addition, the ZnSe-based device exhibits a better photostability than the control device due to the greater ultraviolet (UV) light harvesting of the ZnSe layer, which can efficiently prevent the perovskite film from intense UV-light exposure to avoid associated degradation. Consequently, our results present that a promising ETL can be a potential candidate of the n-type ETL for commercialization of efficient and photostable PKSCs.

# Cysteine Sulfoxidation Increases the Photostability of Red Fluorescent Proteins\_2016

Photobleaching of fluorescent proteins (FPs) is a major limitation to their use in advanced microscopy, and improving photostability remains highly challenging due to limited understanding of its molecular mechanism. Here we discovered a new mechanism to increase FP photostability. Cysteine oxidation, implicated in only photobleaching before, was found to drastically enhance FP photostability to the contrary. We generated a far-red FP mStable by introducing a cysteine proximal to the chromophore. Upon illumination, this cysteine was oxidized to sulfinic and sulfonic acids, enabling mStable more photostable than its ancestor mKate2 by 12-fold and surpassing other far-red FPs. mStable outperformed in laser scanning confocal imaging and super-resolution structured illumination microscopy. Moreover, photosensitization to oxidize a cysteine similarly introduced in another FP mPlum also increased its photostability by 23-fold. This postfolding cysteine sulfoxidation cannot be simply substituted by the isosteric aspartic acid, representing a unique mechanism valuable for engineering better photostability into FPs.

# Photostability Can Be Significantly Modulated by Molecular Packing in Glasses\_2016

While previous work has demonstrated that molecular packing in organic crystals can strongly influence photochemical stability, efforts to tune photostability in amorphous materials have shown much smaller effects. Here we show that physical vapor deposition can substantially improve the photostability of organic glasses. Disperse Orange 37 (DO37), an azobenzene derivative, is studied as a model system. Photostability is assessed through changes in the density and molecular orientation of glassy thin films during light irradiation. By optimizing the substrate temperature used for deposition, we can increase photostability by a factor of 50 relative to the liquid-cooled glass. Photostability correlates with glass density, with density increases of up to 1.3%. Coarse-grained molecular simulations, which mimic glass preparation and the photoisomerization reaction, also indicate that glasses with higher density have substantially increased photostability. These results provide insights that may assist in the design of organic photovoltaics and light-emission devices with longer lifetimes.

# Silylated Coumarin Dyes in Sol−Gel Hosts. 2. Photostability and Sol−Gel Processing\_1998

The photostability characteristics of numerous silylated coumarin dyes within SiO2 xerogels and SiO2:PDMS Polyceram films, and of neat silylated coumarin dye films have been determined and related to the sol−gel processing conditions and host composition. FTIR spectroscopy was used to monitor the hydrolysis reaction rates of the silylated dyes and other Si−alkoxide precursors. The silylated dyes had varying reaction rates depending on the degree of functionality and the linkage between the alkoxide and the dye. Matching the reaction rates between TMOS and the silylated dye was accomplished by prehydrolysis of the silylated dye. The photostability of the dyes in the xerogels was measured by monitoring the drop in fluorescence intensity upon pumping with a N2 laser and also by monitoring the drop in dye absorption upon irradiating the films with a UV lamp. At optimized prehydrolysis times, a silylated coumarin dye (derCoum) within a SiO2 xerogel host demonstrated a 3-fold improvement in long-term photostability compared to its unsilylated counterpart. The use of a silylated dye results in covalently bonding the dye to the host matrix, increasing the probability that the dye will be caged and inhibiting dynamic processes which can lead to photodegradation. CP-MAS 29Si NMR data for a derCoum xerogel confirmed that a large degree of dye bonding occurred. The addition of PDMS to the basic SiO2 xerogel host composition had little effect on the photostability of the dye. The neat dye films showed improved fluorescence photostability with increase in hydrolysis time. These films showed poor photostability upon exposure to UV lamp degradation due to lower thermal degradation resistance and/or thermal conductivity compared to the SiO2 xerogel films.

# Density of States-Based Design of Metal Oxide Thin-Film Transistors for High Mobility and Superior Photostability\_2012

A novel method to design metal oxide thin-film transistor (TFT) devices with high performance and high photostability for next-generation flat-panel displays is reported. Here, we developed bilayer metal oxide TFTs, where the front channel consists of indium-zinc-oxide (IZO) and the back channel material on top of it is hafnium-indium-zinc-oxide (HIZO). Density-of-states (DOS)-based modeling and device simulation were performed in order to determine the optimum thickness ratio within the IZO/HIZO stack that results in the best balance between device performance and stability. As a result, respective values of 5 and 40 nm for the IZO and HIZO layers were determined. The TFT devices that were fabricated accordingly exhibited mobility values up to 48 cm2/(V s), which is much elevated compared to pure HIZO TFTs (∼13 cm2/(V s)) but comparable to pure IZO TFTs (∼59 cm2/(V s)). Also, the stability of the bilayer device (−1.18 V) was significantly enhanced compared to the pure IZO device (−9.08 V). Our methodology based on the subgap DOS model and simulation provides an effective way to enhance the device stability while retaining a relatively high mobility, which makes the corresponding devices suitable for ultradefinition, large-area, and high-frame-rate display applications.

# Merocyanine Dyes with Improved Photostability\_2007

Merocyanine dyes have proven valuable for live cell fluorescence imaging applications, but many structures have been limited by rapid photobleaching. We show that photostability is substantially enhanced for merocyanines having a cyano group at a specific position in the central polymethine chain. Evidence is presented that this is due to reduction in reactivity of the dyes with singlet oxygen. These results point toward cyano-substitution as a general strategy for improving dye performance in imaging applications.

# Promethazine–Montmorillonite Inclusion Complex To Enhance Drug Photostability\_2014

The capability of montmorillonite as a matrix (MONT) to improve the photostability of photolabile drugs has been recently reported. Herein promethazine (PRO), which was chosen as a model drug because of its photodegradation mechanism, was intercalated into this inorganic matrix, and the effects on drug photoprotection were evaluated as well. The hybrid material (MONT-PRO) was successfully prepared with high drug loading and then was characterized by X-ray powder diffraction (XRPD), differential scanning calorimetry (DSC), and FTIR spectroscopy. The spectrophotometric measurements as a function of light exposure time showed that PRO intercalation into montmorillonite markedly improved the drug photostability because a 5-fold-slower degradation rate was determined compared to that measured for PRO in homogeneous solutions; nanosecond transient absorption measurements highlighted that the interaction with the inorganic matrix made negligible the photoionization process of the drug, and its efficiency in producing singlet oxygen was strongly reduced. The MONT-PRO intercalation compound could be easily formulated in gel or ointment media without losing its photostability.

# Solvent-Induced Changes in Photophysics and Photostability of Indole-Naphthyridines\_2015

Molecules that can simultaneously act as hydrogen bond donors and acceptors often exhibit completely different photophysical behavior in protic and aprotic solvents. Formation of multiple hydrogen bonds with, for example, water or alcohols, may lead to enhanced internal conversion; as a result, triplet formation efficiency can be reduced. These changes in photophysical characteristics may influence the photostability. In order to check this hypothesis, we have investigated spectroscopy, photophysics, and changes in photostability caused by interaction with aprotic and protic solvents for 2-(1′H-indol-2′-yl)-[1,5]naphthyridine and 2-(1′H-indol-2′-yl)-[1,8]naphthyridine, molecules with hydrogen bond accepting and donating functionalities. The photostability of these compounds in n-hexane, acetonitrile, and alcohols was studied in the regime of 365 nm irradiation. The photodegradation yield was found to be significantly lower in alcohols. In polar and protic solvents, the presence of two species was detected and attributed to syn and anti rotameric forms; the former are dominant in all environments.

# Butanedithiol Solvent Additive Extracting Fullerenes from Donor Phase To Improve Performance and Photostability in Polymer Solar Cells\_2017

In this work, we demonstrated that the excited poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl)] (PTB7-Th) will be degraded by [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) or photolysis fragment of 1,8-diiodooctane (DIO) in the presence of oxygen and under irradiation of red light. From the previous reports, the fragment of DIO may be involved in the reaction directly. Our work indicates the PC71BM is not directly involved in the reaction, but is acting as a catalyst to promote the reaction of excited donors with oxygen. Thus, PTB7-Th urgently needs a kind of nonresidual iodine-free additive to replace DIO and remove the fullerene from the donor phase at the same time. Taking into consideration PC71BM solubility and boiling point difference between solvent additives and host solvents, 1,4-butanedithiol solvent was selected to fabricate PTB7-Th:PC71BM-based solar cells achieving a best power conversion efficiency (PCE) of 10.2% (8.5% for PTB7:PC71BM). Iodine-free butanedithiol can not only avoid excited polymer reacting with the photolysis fragment of DIO but also suppress the degradation of the excited PTB7-Th caused by synergistic effect between the fullerene and oxygen via extracting the free/trapped PC71BM from the donor phase. Eventually, the film prepared with 1,4-butanedithiol shows higher stability than the film prepared without any additives and much better than the film with DIO in macro-/micromorphology, light absorption, and device performance.

# Simultaneous Improvement of Epalrestat Photostability and Solubility via Cocrystallization: A Case Study\_2017

In this study, we attempt to simultaneously improve the photostability and solubility of epalrestat (a drug used for neuropathy treatment) by preparing epalrestat–betaine zwitterionic cocrystals and characterize the physicochemical property alterations accompanying their formation. Notably, we reveal that the strong hydrogen bonds between epalrestat and betaine molecules in the above cocrystals and the reduced size of the reaction cavity around epalrestat molecules prevent the E,Z to Z,Z photoisomerization of the latter, resulting in improved photostability. Furthermore, the prepared cocrystals exhibit a higher solubility and larger dissolution rate than pure epalrestat crystals due to featuring a layered structure with alternately arranged epalrestat and betaine coformer molecules.

# Meso-Disubstituted Anthracenes with Fluorine-Containing Groups: Synthesis, Light-Emitting Characteristics, and Photostability\_2008

Synthesis, photophysical properties, and photostability of 9,10-disubstituted anthracenes with fluorine-containing groups (FCG) are described. The values of Φf and λem greatly go up by the meso-substitution with FCG, and a nice corelationship between Φf and Aπ (magnitude of π conjugation length in the excited single state) is observed. The C6F5 group at the meso positions exhibits an excellent ability in the photostability as well as in the emission efficiency.

# Photostability of High μβ Electro-Optic Chromophores at 1550 nm\_2004

We present the photostability results of seven novel electro-optic chromophores made to be used in high-speed fiber optic signal modulators. We measured the photobleaching rate of the chromophores at room temperature by using a fiber optic pump−probe technique. Thin polymer film guest−host samples were deposited on the end of SMF-28 fiber pigtails and bleached by using 100 mW of 1550 nm radiation as the pump. The bleaching rate was measured by monitoring the main absorption band of the chromophores by using a 660 nm probe beam that was multiplexed into the fiber pigtail. The relative photostability was reported as a figure of merit which is proportional to the 1/e bleaching lifetime of the chromophore. We found the bleaching rate to increase linearly with incident 1550 nm power at the end of the single-mode fiber up to at least 100 mW. Our results show that the photobleaching rate is reduced dramatically when the test is conducted in an inert atmosphere. We also show that the presence of the singlet oxygen quencher DABCO can be used to increase the lifetime of the chromophore. The effect that chromophore structure and polymer host type have on photostability are also discussed.

# Microfluidic Device for Single-Molecule Experiments with Enhanced Photostability\_2009

A microfluidic device made of polydimethylsiloxane (PDMS) addresses key limitations in single-molecule fluorescence experiments by providing high dye photostability and low sample sticking. Photobleaching is dramatically reduced by deoxygenation via gas diffusion through porous channel walls. Rapid buffer exchange in a laminar sheath flow followed by optical interrogation minimizes surface−sample contacts and allows the in situ addition and combination of other reagents.

# Fluorescent Nanoconjugate Derivatives with Enhanced Photostability for Single Molecule Imaging\_2015

Fluorescence-based imaging techniques critically rely on bright and photostable probes for precise detection of biological molecules. Recently, a new class of multichromophoric probes based on fluorescent dendrimer nanoconjugates (FDNs) was developed for single molecule fluorescence microscopy (SMFM). FDNs are generated by covalent conjugation of multiple fluorescent dyes onto macromolecular polymeric scaffolds and show marked increases in brightness and long-term photostability relative to their single organic dye constituents. Multichromophoric probes, however, are generally known to suffer from transient fluorescence emission intensities and long excursions into dark states. To overcome these issues, photostabilizers can be added to bulk solution, though some small molecule additives may exhibit poor aqueous solubility or biological toxicity. In this work, we develop enhanced FDN derivatives by covalently linking a redox-active photostabilizer (Trolox) directly onto FDN molecular scaffolds. In one approach, multiple organic dyes (Cy5) and Trolox molecules are randomly distributed on dendritic scaffolds in tunable stoichiometric amounts, and in a second approach, Cy5 dyes are covalently linked to Trolox in a precise 1:1 stoichiometry followed by covalent attachment of Cy5–Trolox conjugates onto dendrimers. In all cases, FDN–Trolox conjugates show increases in photostability, brightness, and reduced fluctuations in transient fluorescent intensity relative to FDN probes. Bulk and single molecule photophysical data for FDN probes are compared to single self-healing dye systems such as Cy5–Trolox, and as a proof-of-principle demonstration, we use FDN–Trolox derivatives for bulk immunofluorescence imaging. Overall, our work suggests that self-healed multichromophoric systems such as FDN–Trolox probes present a useful strategy for increasing fluorescent probe photostability.

# Conjugated Polymer Nanoparticles Incorporating Antifade Additives for Improved Brightness and Photostability\_2012

Conjugated polymer nanoparticles with incorporated antifade agents were prepared, and ensemble and single particle measurements showed that incorporation of antifade agents effectively improves the fluorescence quantum yield and photostability of the conjugated polymer nanoparticles, likely by a combination of triplet quenching and suppression of processes involved in photogeneration of hole polarons (cations), which act as fluorescence quenchers. The photostability of conjugated polymer nanoparticles and CdSe quantum dots was compared, at both the ensemble and single particle level. The results provide confirmation of the hypothesis that quenching by photogenerated hole polarons is a key factor limiting the fluorescence quantum yield and maximum emission rate in conjugated polymer nanoparticles. Additionally, the results indicate the involvement of oxygen in photogeneration of hole polarons. The results also provide insight into the origin of quenching processes that could limit the performance of conjugated polymer devices.

# UV Photostability of Metal Phthalocyanines in Organic Solvents\_2003

Kinetic studies of photochemical reactions induced by UV radiation in solutions of metal phthalocyanines have been carried out to determine the factors which might have influenced the stability of photosensitized phthalocyanines. Complexes of the molecular type Mpc, M‘2pc, and Lnpc2 (where M = Li, Mg, Fe, Co, Zn, Pb; M‘= Tl; Ln = rare earth; pc = phthalocyanine ligand, C32H16N82-) were investigated in DMF, DMSO, and pyridine. Progressive decay of the phthalocyanine macrocycle due to absorption of UV light was observed. Phthalimide found in the final photolysis product may indicate some chemically bonded oxygen involved in the solid phthalocyanine material. Fluorescence lifetimes determined for the studied compounds (2.91−5.98 ns) have shown no particular relation to the stability of the excited macrocyclic system. The bonding strength of the photosensitized phthalocyanine moiety appears to rely on typical chemical factors, rather than on the properties of the excited states. Kinetics of the degradation process has proved to depend on the molecular structure of the complex and seems to be controlled by interactions of the macrocycle bridging nitrogen atoms with the solvent molecules. The use of electron acceptor solvents such as DMSO may enhance the molecular stability of phthalocyanines excited by UV radiation. Sandwich-type rare earth diphthalocyanines dissolved in DMSO displayed the highest photostability.

# On-Line Photostability Evaluation System for Chemiluminescence Detection of Phloxine (R-104)\_1997

A simple and rapid on-line analytical system was configured for the evaluation of the photostability of various food coloring agents constantly exposed to light. The screening test for photostability of food coloring agents was carried out in the system consisting of 60 cm of Teflon tubing for ultraviolet (UV) irradiation with a flow rate of mobile phase (water/acetonitrile = 1:1, v/v) at 1 mL/min. When the products derived from photochemical reaction of phloxine (R-104), which is recognized to exhibit chemiluminescence induced by UV irradiation, were separated, several peaks were confirmed on the chromatogram in this system. Furthermore, the peak of chemilumigenics observed on the chromatogram of photon-counting chemiluminescence detection corresponds to the new peaks on the UV chromatogram. Also, the presence of phenoxy radical (g = 2.0061) formed by UV irradiation of R-104 was confirmed with an electron spin resonance spectrometer, indicating a reasonable relationship (r = 0.9041) between the formation of free radical and the chemiluminescence phenomenon.  
Keywords: Photostability; phloxine; chemiluminescence; on-line system; ESR; free radical formation

# Approach of Cocrystallization to Improve the Solubility and Photostability of Tranilast\_2013

The cocrystals and salts of an antiallergic drug, tranilast, were synthesized to improve its solubility and photostability. Two tranilast cocrystals with urea (1) and nicotinamide (2), as well as two salts with cytosine (3) and sodium ion (4), were obtained and characterized by infrared spectra, thermogravimetric analyses, differential scanning calorimetry, and powder and single crystal X-ray diffractions. The results of single crystal structure analyses of 1–3 indicate that tranilast combines amide groups in coformers via R22(8) synthon, resulting in a 1:1 stoichiometry. The complexes showed advantages in terms of solubility and photostability in comparison to pure tranilast. The maximum solubility values of 1–3 in phosphate buffer of pH 6.8 are approximately 1.6, 1.9, and 2.0 times as large as that of tranilast, and the residual of tranilast is 79.5, 92.9, 88.5, 86.2, and 87.4% for tranilast and 1–4, respectively, under the fluorescent lamp irradiation for 96 h.

# Conformation-Dependent Photostability among and within Single Conjugated Polymers\_2015

The relationship between photostability and conformation of 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) conjugated polymers was studied via excitation polarization modulation depth (M) measurements. Upon partial photobleaching, M distributions of collapsed, highly ordered MEH-PPV molecules shifted toward lower values. Conversely, M distributions of MEH-PPV molecules with random coil conformations moved toward higher values after partial photobleaching. Monte Carlo simulations of randomly distributed dipole moments along polymer chains subjected to partial photobleaching revealed that a statistical effect leads to an increase in peak M value. Decreases in M values seen experimentally in the population of MEH-PPV molecules with high M values, however, are due to conformation-dependent photostability within single MEH-PPV polymers. We show that, while folded MEH-PPV molecules are relatively more photostable than extended MEH-PPV molecules in an ensemble, extended portions of particular molecules are more photostable than folded domains within single MEH-PPV molecules.

# Anthracene-Fused BODIPYs as Near-Infrared Dyes with High Photostability\_2011

An anthracene unit was successfully fused to the zigzag edge of a boron dipyrromethene (BODIPY) core by an FeCl3-mediated oxidative cyclodehydrogenation reaction. Meanwhile, a dimer was also formed by both intramolecular cyclization and intermolecular coupling. The anthracene-fused BODIPY monomer 7a and dimer 7b showed small energy gaps (∼1.4 eV) and near-infrared absorption/emission. Moreover, they exhibited high photostability.

# Enhancing Stability and Photostability of CsPbI3 by Reducing Its Dimensionality\_2018

Full inorganic perovskites display their potential to function as stable photovoltaic materials better than the hybrid organic–inorganic perovskites. However, to date, the cesium lead iodide perovskite, which displays a promising absorbance range, has suffered from low stability, which degrades to a nonactive photovoltaic phase rapidly. In this work, we show that the black phase of cesium lead iodide can be stabilized when the perovskite dimensionality is reduced. X-ray diffraction, absorbance, and scanning electron microscopy were used to follow the degradation process of various dimensionalities under room conditions and 1 sun illumination. When comparing the effect on the stability and photostability of cesium lead iodide with linear or aromatic barrier molecules, the aromatic barrier molecule displays better photostability for over 700 h without degradation under continuous 1 sun illumination than does the linear barrier molecule. Theoretical calculations show that the addition of the barrier molecule makes a different charge distribution over the perovskite structure, which stabilizes the CsPbI3 black phase. This work provides the possibility to use the CsPbI3 perovskite as a stable photovoltaic material in solar cells.

# Enhance Effect of Surfactants on the Photoluminescence and Photostability of Water-Soluble Poly(phenylene ethynylene)\_2008

The interaction between the water-soluble anionic fluorescence conjugated polyelectrolytes PPESO3 (poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylethynylene-alt- 1,4-poly(phenylene ethynylene)]) and various surfactants has been studied in aqueous solution by UV−vis absorption spectra and fluorescence spectra. With the addition of surfactants, the aggregations of polymers are broken up. For eliminating the self-quenching effect of the fluorescent polymers, the photoluminescence of PPESO3 is dramatically enhanced. The photoluminescence of PPESO3 can be enhanced 6- to 12-fold with the addition of different surfactants, and at higher concentration of surfactants, the photostability of PPESO3 is also highly increased. A “micelle incorporation model” is proposed to explain the enhancement of photostability. To deeply understand the interaction processes between PPESO3 and surfactants, we systematically studied the fluorescence spectra changes of PPESO3 and the dynamic processes at different CTAB concentrations. All results prove the surfactants can simultaneously enhance the photoluminescence and photostability of water-soluble conjugated polyelectrolytes, and this method is very simple and powerful.

# Influence of Photostability on Single-Molecule Surface Enhanced Raman Scattering Enhancement Factors\_2008

Experimental determinations of enhancement factors in Surface Enhanced Raman Scattering (SERS) are intimately intertwined with the photostability of the probes. We study the effect of the limited photostability in single-molecule SERS (SM-SERS) events and show explicitly how this may result in a large under-estimation of the SERS enhancement factors (EFs) obtained experimentally. To this end, we use the bianalyte technique with isotopically edited probes to provide the best-case scenario for the isolation of single molecule events, and study the statistics of EFs at different incident laser powers. When photobleaching stops playing an important role within the integration time used to capture the spectra, SM-SERS EFs approach an upper bound, which is in agreement with estimations of the EFs within the electromagnetic theory of SERS enhancements. Our results reinforce, in addition, the fact that the highest SM-SERS EFs observed experimentally are typically of the order of ∼1010.

# Toward Stable Deep-Blue Luminescent Colloidal Lead Halide Perovskite Nanoplatelets: Systematic Photostability Investigation\_2019

Colloidal lead halide perovskite nanocrystals and nanoplatelets have emerged as promising semiconductor nanomaterials because of their spectral tunability, facile processability, and bright emission with high color purity. In particular, strong quantum and dielectric confinement make atomically thin colloidal lead bromide perovskite nanoplatelets a favorable candidate for next-generation deep-blue-emitting (λmax = 437 nm) materials. However, poor photostability poses a critical challenge; colloidal nanoplatelets suffer from photobleaching or transformation into thicker, less-confined nanostructures with red-shifted emission upon UV irradiation. In this study, we synthesize deep-blue-emitting organic–inorganic hybrid perovskite nanoplatelets (formula: L2[ABX3]BX4, L: butylammonium and octylammonium, A: methylammonium or formamidinium, B: lead, and X: bromide or iodide) with large lateral dimension (∼1 μm) by ligand-assisted reprecipitation and systematically investigate the factors that affect the photostability of those nanoplatelets. We find that freshness of the prepared precursor solutions for ligand-assisted reprecipitation is critical to obtain better stability with high photoluminescence quantum yield of perovskite nanoplatelets. Photobleaching is found to result from intrinsic instability of the perovskite lattice against UV irradiation in nanoplatelets, whereas transformation into thicker nanostructures results from extrinsic factors—moisture, primarily. Furthermore, we observe that substitution of the organic cation from formamidinium to methylammonium and addition of excess alkylammonium bromide ligands significantly enhance both the ambient and photostability. Lastly, we demonstrate that the dropcast film of methylammonium lead bromide nanoplatelets with excess alkylammonium bromide ligands shows dramatically improved stability both under UV irradiation and under ambient conditions. This study expands our understanding of the factors that affect perovskite nanoplatelet photostability and opens up new possibilities for the fabrication of stable perovskite nanoplatelet-based optoelectronic devices.

# Enhancing the Photostability of Poly(3-hexylthiophene) by Preparing Composites with Multiwalled Carbon Nanotubes\_2011

Poly(3-hexylthiophene) (P3HT) degrades in organic solvents containing dissolved molecular oxygen when irradiated with ultraviolet light. Hence, it is important to develop strategies that can enhance the photostability of P3HT and enhance the device performance. In this work, we report that preparing composites of P3HT with appropriate amounts of multiwalled carbon nanotube (MWCNT) results in superior photostability of P3HT. UV−visible and fluorescence spectroscopy have been used as primary tools to study the photostability of P3HT and its composites. Scanning electron microscopy (SEM) images of the composites display dispersed CNTs being well coated by P3HT. Transmission electron microscopy (TEM) micrographs along with SAED patterns reveal that P3HT coats the CNTs, which is the reason for superior dispersion of the composite. ESR spectroscopy was also performed to pursue and follow the degradation of P3HT. Ten weight percent of MWCNTs in P3HT was found to be the optimum loading amount that results in maximum photostability of the P3HT as compared to the other ratios. This enhanced photostability of P3HT on preparing composites with MWCNT in addition to its easy processability directly from solution makes these composites immensely important for optoelectronic applications.

# Photostability and Photodegradation Processes in Colloidal CsPbI3 Perovskite Quantum Dots\_2018

All-inorganic CsPbI3 perovskite quantum dots (QDs) have attracted intense attention for their successful application in photovoltaics (PVs) and optoelectronics that are enabled by their superior absorption capability and great photoluminescence (PL) properties. However, their photostability remains a practical bottleneck and further optimization is highly desirable. Here, we studied the photostability of as-obtained colloidal CsPbI3 QDs suspended in hexane. We found that light illumination does induce photodegradation of CsPbI3 QDs. Steady-state spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, and transient absorption spectroscopy verified that light illumination leads to detachment of the capping agent, collapse of the CsPbI3 QD surface, and finally aggregation of surface Pb0. Both dangling bonds containing surface and Pb0 serve as trap states causing PL quenching with a dramatic decrease of PL quantum yield. Our work provides a detailed insight about the correlation between the structural and photophysical consequences of the photodegradation process in CsPbI3 QDs and may lead to the optimization of such QDs toward device applications.

# Photostability of Gold Nanorods upon Endosomal Confinement in Cultured Cells\_2017

The photoinstability of plasmonic particles remains one remarkable obstacle before their clinical penetration as powerful contrast agents, for instance, in photoacoustic imaging. In particular, gold nanorods easily revert to nanospheres and so lose their best optical features under exposure to few-nanoseconds-long laser pulses. While this issue is attracting much attention and stimulating ad hoc solutions, such as the addition of rigid shells, the biological environment may cause even more instability. For instance, a frequent outcome of the interaction between this type of particles and malignant or immune cells is their tight confinement into endocytic vesicles. In this study, we assess whether this configuration may make an adverse impact on the photostability of gold nanorods, due to the effect of heat confinement. We compare experimental measurements from a limited set of representative samples and verify their relevance by the use of numerical simulations. Under conditions that are typical for photoacoustic microscopy, we estimate the threshold fluence for the onset of photoinstability to remain around 7 mJ·cm–2, independent of the distance among neighboring particles, within accessible limits. Then, we simulate the effect of pulse duration in our model of endocytic confinement. Only in a μs regime of lesser potential for biomedical optics do we predict this configuration to destabilize the gold nanorods, still by as little as 15–20%. Our results span from the femtosecond up to the continuous wave regimes of irradiation and suggest that the biological interface does not pose a major threat on the photostability of plasmonic particles for most biomedical applications, including the photoacoustic imaging and photothermal ablation of cancer.

# Enhanced Photostability of Monascus Pigments Derived with Various Amino Acids via Fermentation\_2005

The photostability of 18 amino acid derivatives from monascus pigment was tested under various physical and chemical conditions. Under sunlight, the half-life of derivatives was increased to 1.45−5.58 h, corresponding to a 6−25-fold improvement over a control red pigment (0.22 h). The degradation of pigment derivatives followed a first-order reaction, and the pigment stability increased with an increasing concentration while it decreased with both an increase and decrease in pH from 7. The stabilities of derivatives decreased in descending order in hexane, ethanol, propanol, methanol, ethyl ether, distilled water, chloroform, and acetonitrile. Pigment stability under UV light (365 nm) showed a pattern similar to stability after exposure to sunlight. After 30 days of incubation at 30 °C, more than 80% of the initial derivative contents remained while only 29% of the control red remained. The differences in degradation patterns that control red gradually changed to brown whereas the phenylalanine derivative remained a weak red were confirmed by HPLC analysis.  
Keywords: Monascus; pigment; amino acid derivatives; photostability; kinetics

# Photodesorption and Photostability of Acetone Ices: Relevance to Solid Phase Astrochemistry\_2014

Acetone, one of the most important molecules in organic chemistry, also a precursor of prebiotic species, was found in the interstellar medium associated with star-forming environments. The mechanisms proposed to explain the gas phase abundance of interstellar acetone are based on grain mantle chemistry. High energy photons coming from the stellar radiation field of the nearby stars interact with the ice mantles on dust grains leading to photoionization, photodissociation, and photodesorption processes. In this work we investigate the photodesorption and the photostability of pure acetone ices due to soft X-ray impact. Absolute desorption yields per photon impact for the main positive ionic fragments were determined at the O 1s resonance energy (531.4 eV). The photostability of acetone ice was studied by exposure to different irradiation doses with a white beam of synchrotron radiation. The degradation of the ice was monitored by NEXAFS around the O 1s threshold. From this study we determine the photodissociation cross-section to be about 1.5 × 10–17 cm2 which allowed us to estimate the half-life for acetone ice in astrophysical environments where soft X-rays play an important role in chemical processes.

# Perylene-Fused BODIPY Dye with Near-IR Absorption/Emission and High Photostability\_2011

A N-annulated perylene unit was successfully fused to the meso- and β-positions of a boron dipyrromethene (BODIPY) core. The newly synthesized BODIPY dye 1b exhibits intensified near-infrared (NIR) absorption and the longest emission maximum ever observed for all BODIPY derivatives. In addition, this dye possesses excellent solubility and photostability, beneficial to practical applications.

# Chemoselective Trifluoroethylation Reactions of Quinazolinones and Identification of Photostability\_2019

Herein, we report chemoselective trifluoroethylation routes of unmasked 2-arylquinazolin-4(3H)-ones using mesityl(2,2,2-trifluoroethyl)iodonium triflate at room temperature. Homologous C-, O-, and N-functionalized subclasses are accessed in a straightforward manner with a wide substrate scope. These chemoselective branching events are driven by Pd-catalyzed ortho-selective C–H activation at the pendant aryl ring and base-promoted reactivity modulation of the amide group, leveraging the intrinsic directing capability and competing pronucleophilicity of the quinazolin-4(3H)-one framework. Furthermore, outstanding photostability of the quinazolin-4(3H)-one family associated with nonradiative decay is presented.

# Near-Infrared Fluorescent Thienothiadiazole Dyes with Large Stokes Shifts and High Photostability\_2017

A series of near-infrared (NIR) organic emissive materials were synthesized and the photophysical properties analyzed. The donor–acceptor–donor materials were designed with thienopyrazine and thienothiadiazole acceptor groups with thiophene-, furan-, and triphenylamine-based donor groups. The absorption and emission spectra were found to be widely tunable on the basis of the donor and acceptor groups selected. Computational analysis confirms these materials undergo an intramolecular charge-transfer event upon photoexcitation. Large Stokes shifts of ∼150 nm were observed and rationalized by computational analysis of geometry changes in the excited state. Fluorescence studies on the dye series reveal maximum peak emission wavelengths near 900 nm and a quantum yield exceeding 16% for 4,6-bis(2-thienyl)thieno[3,4-c][1,2,5]thiadiazole. Additionally, several dyes were found to have reasonable quantum yields within this NIR region (>1%), with emission wavelengths reaching 1000 nm at the emission curve onset. Photostability studies were conducted on these materials in an ambient oxygen environment, revealing excellent stability in the presence of oxygen from all the dyes studied relative to a benchmark cyanine dye (ICG) during photoexcitation with exceptional photostability from the 4,6-bis(5′-dodecyl-[2,2′-bithiophene]-5-yl)thieno[3,4-c][1,2,5]thiadiazole derivative.

# Fluorescence and Electrochemiluminescence of Luminol-Reduced Gold Nanoparticles:  Photostability and Platform Effect\_2008

Water-soluble gold nanoparticles (AuNPs) capped with both fluorescent (FL) 3-aminophthalate (APA) and electrochemiluminescent (ECL) luminol molecules were described in our previous work. The synthetic and characteristic efforts of these functionalized AuNPs (lumAuNPs) were subsequently followed by investigations of their FL and ECL properties, as reported in the present work. It was observed that the FL intensity of a single gold nanoparticle was 70 times brighter than that of one free APA molecule, even though 91% of the FL emission of APA molecules on the surfaces of AuNPs was inhibited by gold cores through both intra- and interparticle quenching effects. Moreover, the photobleaching of surface-bound APA molecules was found to be dramatically inhibited compared with that of free ones in carbonate buffer. The improvement of photostability was attributed to the reactive AuNPs which acted as radical scavengers to protect the surface-bound APA molecules from oxidation by carbonate radicals. Furthermore, as-prepared lumAuNPs could react with cysteine to produce strong electrochemiluminescence, which was enhanced by 20-fold compared with that in the absence of cysteine. The experimental results suggested that luminol and cysteine were coadsorbed on the gold nanoparticle platform via Au−N and Au−S interactions, respectively. The shorter distance between reactant molecules by overcoming the electrostatic repulsion, that is, platform effect, was proposed to be responsible for the ECL enhancement. Combined with the biocompatibility of gold cores, the brighter FL emission, enhanced photostability, and stronger ECL intensity may make as-prepared lumAuNPs promising FL and ECL biomarkers for their applications in biosensors and bioimaging.

# Improving the Photostability of Ultrasmall Au Clusters via a Combined Strategy of Surface Engineering and Interfacial Modification\_2019

Photostability is a critical issue for evaluating the use of photocatalysts to realize large-scale implementation of solar energy conversion. Recently emerged ultrasmall gold (Au) clusters with distinctive physicochemical properties have been regarded as visible-light photosensitizers for photoredox catalysis, whereas the poor stability under visible-light exposure greatly restricts their photocatalytic applications. Herein, we provide a proof-of-concept study on enhancing the photostability of ultrasmall Au clusters via a combined strategy of surface engineering and interfacial modification. The photostability of Au clusters on the surface of TiO2 nanosheets with less hydroxyl group can be improved to some extent as compared to that on TiO2 nanoparticles with abundant hydroxyl groups under continuous visible-light irradiation (λ > 420 nm). Moreover, the subsequent modification of branched polyethylenimine (BPEI) between TiO2 nanosheets and Au clusters further improves their photostability upon light illumination. Consequently, the as-constructed TiO2 nanosheet–BPEI–Au cluster composites exhibit stable visible-light activity toward Cr(VI) photoreduction. It is hoped that the joint strategy via surface engineering and interfacial modification provides a facile guideline for stabilizing ultrasmall Au clusters toward targeting applications in the photoredox catalysis process.

# A Doorway State Leads to Photostability or Triplet Photodamage in Thymine DNA\_2008

Ultraviolet irradiation of DNA produces electronic excited states that predominantly eliminate the excitation energy by returning to the ground state (photostability) or following minor pathways into mutagenic photoproducts (photodamage). The cyclobutane pyrimidine dimer (CPD) formed from photodimerization of thymines in DNA is the most common form of photodamage. The underlying molecular processes governing photostability and photodamage of thymine-constituted DNA remain unclear. Here, a combined femtosecond broadband time-resolved fluorescence and transient absorption spectroscopies were employed to study a monomer thymidine and a single-stranded thymine oligonucleotide. We show that the protecting deactivation of a thymine multimer is due to an ultrafast single-base localized stepwise mechanism where the initial excited state decays via a doorway state to the ground state or proceeds via the doorway state to a triplet state identified as a major precursor for CPD photodamage. These results provide new mechanistic characterization of and a dynamic link between the photoexcitation of DNA and DNA photostability and photodamage.

# Comparative Analysis of Methods for Enhancement of the Photostability of [email protected] QD Colloid Solutions\_2017

The employment of colloid quantum dots in a number of applications is limited by their instability under light irradiation. Additional methods of photostability enhancement of UV+visible-irradiated TGA-stabilized CdTe quantum dots are investigated. Photostability enhancement was observed via either addition of sodium sulphite in the role of chemical oxygen absorber or addition of 1% gelatin, or, finally, by additional stabilization by bovine serum albumine (BSA). The latter method is the most promising, since it not only enhances the quantum dots’ photostability but also makes them more biocompatible and extends the possibilities of their biological applications.

# Quantitative Comparison of Organic Photovoltaic Bulk Heterojunction Photostability Under Laser Illumination\_2014

The photostability of bulk heterojunction organic photovoltaic films containing a polymer donor and a fullerene-derivative acceptor was examined using resonance Raman spectroscopy and controlled laser power densities. The polymer donors were poly(3-hexylthiophene-2,5-diyl) (P3HT), poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), or poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7). Four sample preparation methods were studied: (i) thin or (ii) thick films with fast solvent evaporation under nitrogen, (iii) thick films with slow solvent evaporation under nitrogen, and (iv) thin films dried under nitrogen followed by thermal annealing. Polymer order was assessed by monitoring a Raman peak’s full width at half-maximum and location as a function of illumination time and laser power densities from 2.5 × 103 to 2.5 × 105 W cm–2. Resonance Raman spectroscopy measurements show that before prolonged illumination, PCDTBT and PTB7 have the same initial order for all preparation conditions, while P3HT order improves with slow solvent drying or thermal annealing. All films exhibited changes to bulk heterojunction structure with 2.5 × 105 Wcm–2 laser illumination as measured by resonance Raman spectroscopy, and atomic force microscopy images show evidence of sample heating that affects the polymer over an area greater than the illumination profile. Photostability data are important for proper characterization by techniques involving illumination and the development of devices suitable for real-world applications.

# Study on Photoluminescence Quenching and Photostability Enhancement of MEH-PPV by Reduced Graphene Oxide\_2012

In conjugated polymer based photovoltaic devices, efficient charge transfer and photostability of the fluorescence polymer are two essential properties, which could be responsible for better performance and longer lifetime of the device. Hence, it is of great importance to explore strategies that can enhance the exciton separation and improve the photostability of polymers. In this work, composites of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) participated by appropriate amounts of reduced graphene oxide (r-GO), which leads to a significant photoluminescence quenching as well as superior photostability of MEH-PPV, have been investigated. The photoluminescence quenching and photostability of MEH-PPV/r-GO composites have been observed by UV–visible and fluorescence spectroscopy. From transient fluorescence spectrum, the mechanism of photoluminescence quenching has been confirmed to be static quenching, which is caused by electron transfer at the interface of the composite. Furthermore, we propose that this very efficient photoinduced excitation electron transfer from MEH-PPV to r-GO results in protecting MEH-PPV from further chemical degradation reaction. This work shows that graphene is promising as both an electron acceptor and light stabilizer for applications in optoelectronics devices.

# Acid Blue 129 and Salicylate Cointercalated Layered Double Hydroxides: Assembly, Characterization, and Photostability\_2014

Acid Blue 129 (AB129) and salicylate have been cointercalated into the interlayer galleries of ZnAl layered double hydroxides (LDHs) through a coprecipitation method to prepare organic–inorganic hybrid pigments with improved photostability. The prepared hybrids were characterized by XRD, FTIR spectroscopy, SEM, TG-DTG-DTA, UV–vis spectroscopy, and CIE 1976 L\*a\*b\* color scales. The results show the successful cointercalation of AB129 and salicylate into the interlayer space of LDHs, forming a new kind of organic–inorganic hybrid pigment, and reveal that intercalation into the interlayer of LDHs can slightly improve the thermal stability of AB129 as a result of the protection offered by LDH layers. The AB129/salicylate molar ratio plays an important part in the color properties of the hybrid pigment. The cointercalation of salicylate can efficiently enhance the photostability of AB129 by absorbing harmful UV rays. Therefore, the cointercalation of AB129 and salicylate into the interlayer of ZnAl LDHs can effectively produce organic–inorganic hybrid pigments with enhanced photostability.

# High Photostability in Nonconventional Coumarins with Far-Red/NIR Emission through Azetidinyl Substitution\_2018

Replacement of electron-donating N,N-dialkyl groups with three- or four-membered cyclic amines (e.g., aziridine and azetidine, respectively) has been described as a promising approach to improve some of the drawbacks of conventional fluorophores, including low fluorescent quantum yields (ΦF) in polar solvents. In this work, we have explored the influence of azetidinyl substitution on nonconventional coumarin-based COUPY dyes. Two azetidine-containing scaffolds were first synthesized in four linear synthetic steps and easily transformed into far-red/NIR-emitting fluorophores through N-alkylation of the pyridine moiety. Azetidine introduction in COUPY dyes resulted in enlarged Stokes’ shifts with respect to the N,N-dialkylamino-containing parent dyes, but the ΦF were not significantly modified in aqueous media, which is in contrast with previously reported observations in other fluorophores. However, azetidinyl substitution led to an unprecedented improvement in the photostability of COUPY dyes, and high cell permeability was retained since the fluorophores accumulated selectively in mitochondria and nucleoli of HeLa cells. Overall, our results provide valuable insights for the design and optimization of novel fluorophores operating in the far-red/NIR region, since we have demonstrated that three important parameters (Stokes’ shifts, ΦF, and photostability) cannot be always simultaneously addressed by simply replacing a N,N-dialkylamino group with azetidine, at least in nonconventional coumarin-based fluorophores.

# Improving the Photostability of Red- and Green-Emissive Single-Molecule Fluorophores via Ni2+ Mediated Excited Triplet-State Quenching\_2016

Methods to improve the photostability/photon output of fluorophores without compromising their signal stability are of paramount importance in single-molecule fluorescence (SMF) imaging applications. We show herein that Ni2+ provides a suitable photostabilizing agent for three green-emissive (Cy3, ATTO532, Alexa532) and three red-emissive (Cy5, Alexa647, ATTO647N) fluorophores, four of which are regularly utilized in SMF studies. Ni2+ works via photophysical quenching of the triplet excited state eliminating the potential for reactive intermediates being formed. Measurements of survival time, average intensity, and mean number of photons collected for the six fluorophores show that Ni2+ increased their photostability 10- to 45-fold, comparable to photochemically based systems, without compromising the signal intensity or stability. Comparative studies with existing photostabilizing strategies enabled us to score different photochemical and photophysical stabilizing systems, based on their intended application. The realization that Ni2+ allowed achieving a significant increase in photon output both for green- and red-emissive fluorophores positions Ni2+ as a widely applicable tool to mitigate photobleaching, most suitable for multicolor single-molecule fluorescence studies.

# Pt/[email protected] Nanocable with Dual-Enhanced Photocatalytic Performance and Superior Photostability\_2017

To improve the photocatalytic activity and photostability of ZnO, a novel cable-like Pt/ZnO@C composite is successfully fabricated by coating a 3–5 nm hydrothermal carbon (HTC) layer on the surface of the Pt nanoparticle-modified ZnO nanowire. After investigating the optical and photoelectrochemical performance in detail, it is found that the Pt/ZnO@C nanocable shows a dual-enhanced migration efficiency for the photoinduced surface electrons, distributing to the modified Pt nanoparticles and the coated HTC layer. Consequently, the Pt/ZnO@C nanocable exhibits a dual-enhanced photocatalytic activity for the degradation of various organic pollutants under the UV light irradiation. The coated HTC layer can also play a role in suspending the ZnO photocorrosion and significantly improves the photostability of the Pt/ZnO@C nanocable. Furthermore, the photocatalysis and photocorrosion mechanism of the Pt/ZnO@C nanocable is proposed and discussed in terms of its structural feature and photoelectrochemical property. The resultant Pt/ZnO@C nanocable with the unique HTC layer-coated structure will probably stimulate to design and synthesize more HTC-hybridized composites with a superior photocatalytic or photoelectrocatalytic performance.

# Aziridinyl Fluorophores Demonstrate Bright Fluorescence and Superior Photostability by Effectively Inhibiting Twisted Intramolecular Charge Transfer\_2016

Replacing conventional dialkylamino substituents with a three-membered aziridine ring in naphthalimide leads to significantly enhanced brightness and photostability by effectively suppressing twisted intramolecular charge transfer formation. This replacement is generalizable in other chemical families of fluorophores, such as coumarin, phthalimide, and nitrobenzoxadiazole dyes. In highly polar fluorophores, we show that aziridinyl dyes even outperform their azetidinyl analogues in aqueous solution. We also proposed one simple mechanism that can explain the vulnerability of quantum yield to hydrogen bond interactions in protonic solvents in various fluorophore families. Such knowledge is a critical step toward developing high-performance fluorophores for advanced fluorescence imaging.

# Effects of Backbone Planarity and Tightly Packed Alkyl Chains in the Donor–Acceptor Polymers for High Photostability\_2016

The photostability of donor–acceptor (D–A) polymers remains a critical issue despite recent improvements in the power conversion efficiencies (PCEs) of organic photovoltaic (OPV) cells. We report the synthesis of three highly photostable polymers (PDTBDT-BZ, PDTBDT-BZF, and PDTBDT-BZF2) and their suitability for use in high-performance OPV cells. Under 1 sunlight of illumination in air for 10 h, these polymer films demonstrated remarkably high photostability compared to that of PTB7, a representative polymer in the OPV field. While the PDTBDT-BZ, PDTBDT-BZF, and PDTBDT-BZF2 polymer films maintained 97, 90, and 96% photostability, respectively, a PTB7 film exhibited only 38% photostability under the same conditions. We ascribed the high photostability of the polymers to both the intrinsically photostable chemical moieties and the dense packing of alkyl side chains and planar backbone polymer chains, which prevents oxygen diffusion into the PDTBDT-BZ films. This work demonstrates the high photostability of planar PDTBDT-BZ series polymers composed of photostable DTBDT and BZ moieties and suggests a design rule to synthesize highly photostable photovoltaic materials.

# Photostability of Natural Orange−Red and Yellow Fungal Pigments in Liquid Food Model Systems\_2009

The variation in the photostability among the currently authorized natural pigments limits their application span to a certain type of food system, and more robust alternatives are being sought after to overcome this problem. In the present study, the photostability of an orange−red and a yellow fungal pigment extract produced by ascomycetous fungi belonging to the genera Penicillium and Epicoccum, respectively, were studied in a soft drink model medium and in citrate buffer at low and neutral pH. The quantitative and qualitative color change pattern of the fungal pigment extracts indicated an enhanced photostability of fungal pigment extracts compared to the commercially available natural colorants Monascus Red and turmeric used as controls. Yellow components of the orange−red fungal pigment extract were more photostable than the red components. Chemistry of the photodegradation of the orange−red pigment extract was studied by high-performance liquid chromatography−diode array detection−mass spectrometry (HPLC−DAD−MS), and a light-induced formation of a structural analogue of sequoiamonascin C, a Monascus-like polyketide pigment discovered in the extract of Penicillium aculeatum IBT 14263 on yeast extract sucrose (YES) medium, was confirmed in the soft drink medium at pH 7.

# Photostability via a Sloped Conical Intersection:  A CASSCF and RASSCF Study of Pyracylene\_2005

An extensive ab initio study of the ground- and excited-state potential energy surfaces of pyracylene is presented in this work. CASSCF calculations show that there is an accessible sloped S0/S1 conical intersection, which leads to ultrafast internal conversion and explains the observed photostability. RASSCF calculations (using a well-defined subset of the CASSCF configurations) are shown to be able to reproduce CASSCF results satisfactorily and will therefore be useful for larger systems where CASSCF is currently too expensive. MRCI and MRPT2 energy corrections are computed to assess the ionic character of the excited states. Finally, MMVB calculations are also benchmarked against CASSCF, to assess the reliability of this parametrized method for excited states of large conjugated polycyclic aromatic hydrocarbons.

# Enhancing the Photostability of Arylvinylenebipyridyl Compounds as Fluorescent Indicators for Intracellular Zinc(II) Ions\_2015

Arylvinylenebipyridyl (AVB) ligands are bright, zinc(II)-sensitive fluoroionophores. The applicability of AVBs as fluorescent indicators for imaging cellular zinc(II), however, is limited by low photostability, partially attributable to the photoisomerization of the vinylene functionality. Two configurationally immobilized (i.e., “locked”) AVB analogues are prepared in this work. The zinc(II)-sensitive photophysical properties and zinc(II) affinities of both AVBs and their locked analogues are characterized in organic and aqueous media. The zinc(II) sensitivity of the emission is attributed to the zinc(II)-dependent energies of the charge transfer excited states of these compounds. The configurationally locked ligands have improved photostability, while maintaining the brightness and zinc(II) sensibility of their AVB progenitors. The feasibility of the “locked” AVB analogues with improved photostability for imaging intracellular Zn(II) of eukaryotic cells using laser confocal fluorescence microscopy is demonstrated.

# Photostability of UV Screeners in Polymers and Coatings\_1996

All major classes of commercially available UV screeners undergo photodegradation at quantum yields on the order of 1 X 10M-6 in polar matrices. The rates obey zero-order kinetics in the high-absorption range and are highly dependent on the nature of the matrix. Typical rates of photodegradation for screeners in cast polymethyl methacrylate films are on the order of 0.3 to 0.7 absorption units per year of outdoor exposure and 0.2 to 0.5 absorption units per 1000 h of xenon-arc or QUV exposure. Concentration of the screener appears to play little role. The presence of hindered amine light stabilizers and the nature of the light source might affect the rate of degradation of the matrix. Rapidly degrading matrices seem to cause rapid destruction of the screeners.

# Photostability of Kainic Acid in Seawater\_2007

The environmental degradation of a mixture of domoic acid (DA) and kainic acid (KA) in seawater with and without added transition metals is reported. The association constants for kainic acid with FeIII and CuII were determined using 1H nuclear magnetic resonance (NMR; K1,FeIII = 2.27 × 1012, K2,FeIII = 8.99 × 108, K1,CuII = 1.38 × 1010, and K2,CuII = 4.35 × 107). The photochemical half-life of kainic acid has been determined to be significantly longer (40–100 h) than that of domoic acid in corresponding marine systems (12–34 h). The significance of this finding was highlighted by a comparison of the quantification of a mixture of kainic and domoic acids during photodegradation by liquid chromatography–tandem mass spectrometry (LC–MS/MS) techniques and the widely used competitive enzyme-linked immunosorbent assay (cELISA; Biosense Laboratories) method. The MS-based analysis showed that approximately 50% of the DA was photodegraded within 15 h. In contrast, the domoic acid cELISA assay reported that the concentration essentially remained unchanged over this period. The possibility of interference from naturally occurring kainic acid during cELISA measurements could lead to the overestimation of total domoic acid, especially if they occur in mixtures in sunlit waters.

# Photostability Enhancement of Fluorenone-Based Two-Photon Fluorescent Probes for Cellular Nucleus Monitoring and Imaging\_2016

A series of fluorenone-based two-photon fluorescent probes with high photostability for nucleus imaging are prepared and developed. The one- and two-photon photophysical properties exhibit these new probes possess 0.448–0.634 of fluorescence quantum yields and 469–495 GM of two-photon absorption cross sections at 800 nm femtosecond laser excitation. The luminescence “turn-on” experiment in buffer solutions indicates that 35-fold of fluorescence intensity and 68-fold fluorescence quantum yield enhancement appear between new probes and calf thymus DNA. In the nuclear double-staining experiment, the high mean colocalization coefficients of 0.92–0.96 between new probes and nuclear labeling dye Hoechst 33342 are acquired, demonstrating excellent nuclear localization in 3T3 cells. The counterstain studies by introducing commercial mitochondrial staining reagent MTR and nuclear staining dye DAPI further show good membrane permeability and counterstain compatibility in multicolor cell labeling application. The photostability studies show that 3000 s of observation time and 0.028%/s–0.03%/s of mean fluorescence attenuation rates under persistent laser irradiation in two-photon nuclear imaging are achieved. Meanwhile, the cause of fluorescence attenuation in the photostability test for cellular nuclei monitoring are discussed as well.

# Carboxyl BODIPY Dyes from Bicarboxylic Anhydrides: One-Pot Preparation, Spectral Properties, Photostability, and Biolabeling\_2009

New fluorescent dyes based on 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and functionalized with a free carboxyl group have been conveniently synthesized from pyrroles and dicarboxylic anhydrides in one-pot reactions. Their spectral properties in different solvents showed little effect of solvatochromism (<10 nm). The methyl groups on the BODIPY skeleton benefit the fluorescence quantum yields (Φf up to 0.80 in water) but affect the photostability of the dyes. Photooxidation and photodegradation experiments suggest that dyes 1a and 2a exhibit excellent photostability, especially in water, and several factors were taken into account to elucidate the experimental phenomena. Dyes 1c and 2c, derived from 1a and 2a via the esterification of NHS (N-hydroxysuccinimidyl ester), can be easily acquired in high yields (>90%). Single crystal X-ray structures of dyes 2c and 3a are also obtained and discussed. The fluorescence labeling of BSA and followed prestaining method for gel electrophoresis of BSA demonstrate that the protein can be directly observed by naked eyes at as low as 2 ng level under a normal UV fluorescence electrophorogram gel image system.

# Enhancing Luminescence and Photostability of CsPbBr3 Nanocrystals via Surface Passivation with Silver Complex\_2018

We demonstrate that Ag(I) complex can fix bromide on the nanocrystal surface, reduce surface trap density, and as a result efficiently passivate the surface of CsPbBr3 nanocrystals. This passivation makes the photoluminescence (PL) intensity increase several times. The PL kinetics study clearly shows that the decay lifetime increased after the passivation. TEM and XPS analyses demonstrated the existence of Ag on the nanocrystal surface. In addition, we utilize single-particle spectroscopy combined with in situ light analysis to further confirm the PL enhancement effect. On the contrary, the passivation leads to the extraordinary photostability of CsPbBr3 nanocrystals, with 80% PL intensity retained after UV illumination for 5 days under ambient conditions.

# Mordant Yellow 3 Anions Intercalated Layered Double Hydroxides: Preparation, Thermo- and Photostability\_2012

Mordant yellow 3 (MY3) anions have been intercalated into Zn-Al layered double hydroxides (LDH) to produce a novel intercalation compound pigment by a direct coprecipitation method. The prepared composite was characterized by various techniques such as powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetry and differential thermal analysis (TGA-DTA), and UV–vis spectroscopy. The obtained results show that MY3 anions were intercalated into the interlayer spacing of LDH as observed from PXRD and FT-IR. Furthermore, the intercalation of MY3 anions into the LDH markedly enhances the thermo- and photostability of MY3, which may enlarge the practical application fields of MY3 dye.

# Congeners of Pyrromethene-567 Dye: Perspectives from Synthesis, Photophysics, Photostability, Laser, and TD-DFT Theory\_2015

In an attempt to develop photostable and efficient BODIPY (PM) dyes for use in liquid dye lasers, three new congeners of widely used laser dye, PM567, were synthesized and their photophysical properties in various organic solvents, laser performances, and photostabilities in a selected solvent, 1,4-dioxane, have been investigated using a frequency doubled Q-switched (10 Hz) Nd:YAG laser at 532 nm. The results of photostability study in nonpolar 1,4-dioxane revealed the remarkable enhancement in stability of the novel dyes compared to that of PM567 as well as improved laser performances. Cyclic voltammetry study strongly supports the observed enhancement in photostability of the novel dyes compared to that of PM567. The observed properties of the novel dyes in relation to those of PM567 have been rationalized by extensive use of DFT and TD-DFT using the B3LYP/6-31G(d) method of theory.

# Synthesis and Photostability of Unimolecular Submersible Nanomachines: Toward Single-Molecule Tracking in Solution\_2016

The synthesis and photophysical properties of a series of photostable unimolecular submersible nanomachines (USNs) are reported as a first step toward the analysis of their trajectories in solution. The USNs have a light-driven rotatory motor for propulsion in solution and photostable cy5-COT fluorophores for their tracking. These cy5-COT fluorophores are found to provide an almost 2-fold increase in photostability compared to the previous USN versions and do not affect the rotation of the motor.

# Proton/Hydrogen Transfer Mechanisms in the Guanine–Cytosine Base Pair: Photostability and Tautomerism\_2012

Proton/hydrogen-transfer processes have been broadly studied in the past 50 years to explain the photostability and the spontaneous tautomerism in the DNA base pairs. In the present study, the CASSCF/CASPT2 methodology is used to map the two-dimensional potential energy surfaces along the stretched NH reaction coordinates of the guanine–cytosine (GC) base pair. Concerted and stepwise pathways are explored initially in vacuo, and three mechanisms are studied: the stepwise double proton transfer, the stepwise double hydrogen transfer, and the concerted double proton transfer. The results are consistent with previous findings related to the photostability of the GC base pair, and a new contribution to tautomerism is provided. The C-based imino-oxo and imino-enol GC tautomers, which can be generated during the UV irradiation of the Watson–Crick base pair, have analogous radiationless energy-decay channels to those of the canonical base pair. In addition, the C-based imino-enol GC tautomer is thermally less stable. A study of the GC base pair is carried out subsequently taking into account the DNA surroundings in the biological environment. The most important stationary points are computed using the quantum mechanics/molecular mechanics (QM/MM) approach, suggesting a similar scenario for the proton/hydrogen-transfer phenomena in vacuo and in DNA. Finally, the static model is complemented by ab initio dynamic simulations, which show that vibrations at the hydrogen bonds can indeed originate hydrogen-transfer processes in the GC base pair. The relevance of the present findings for the rationalization of the preservation of the genetic code and mutagenesis is discussed.

# Improving Dissolution and Photostability of Vitamin K3 via Cocrystallization with Naphthoic Acids and Sulfamerazine\_2015

Menadione (MD), also known as vitamin K3, has been widely applied in fortified food, feed, and the nutrition industry for its antihemorrhagic activity. However, the poor photostability in the solid state has greatly affected its biological performance and limited its applications. With the objective to alter the topochemical photoreactivity, a cocrystallization approach was employed, and three MD cocrystals with naphthoic acids and sulfamerazine were designed and prepared. Single crystal structures were determined, and solid-state characterization were performed. Solid-state UV–vis spectra revealed a significant red-shift of UV absorption in the cocrystal solids resulting in variant color differences. These physicochemical changes may be attributed to the enhanced π···π interactions and change-transfer interactions within these molecular complexes. More importantly, the newly synthesized cocrystals displayed better dissolution behavior and superior photostability with respect to MD itself. No obvious degradation was observed under stressed photoirradiation conditions. These findings may provide new possibilities to the application of this key vitamin.

# Synthesis and Photostability of Poly(p-phenylenevinylene-borane)s\_2009

The cyanine dye thiazole orange (TO) is a well-known fluorogenic stain for DNA and RNA, but this property precludes its use as an intracellular fluorescent probe for non-nucleic acid biomolecules. Further, as is the case with many cyanines, the dye suffers from low photostability. Here, we report the synthesis of a bridge-substituted version of TO named α-CN-TO, where the central methine hydrogen of TO is replaced by an electron withdrawing cyano group, which was expected to decrease the susceptibility of the dye toward singlet oxygen-mediated degradation. An X-ray crystal structure shows that α-CN-TO is twisted drastically out of plane, in contrast to TO, which crystallizes in the planar conformation. α-CN-TO retains the fluorogenic behavior of the parent dye TO in viscous glycerol/water solvent, but direct irradiation and indirect bleaching studies showed that α-CN-TO is essentially inert to visible light and singlet oxygen. In addition, the twisted conformation of α-CN-TO mitigates nonspecific binding and fluorescence activation by DNA and a previously selected TO-binding protein and exhibits low background fluorescence in HeLa cell culture. α-CN-TO was then used to select a new protein that binds and activates fluorescence from the dye. The new α-CN-TO/protein fluoromodule exhibits superior photostability to an analogous TO/protein fluoromodule. These properties indicate that α-CN-TO will be a useful fluorogenic dye in combination with specific RNA and protein binding partners for both in vitro and cell-based applications. More broadly, structural features that promote nonplanar conformations can provide an effective method for reducing nonspecific binding of cationic dyes to nucleic acids and other biomolecules.

# Twisted Cyanines: A Non-Planar Fluorogenic Dye with Superior Photostability and its Use in a Protein-Based Fluoromodule\_2012

Composite systems where quantum dots (QDs) are combined with other nanomaterials (e.g., gold nanorods) in aqueous solutions have attracted broad attention—both for their potential in applications and for studies of fundamental processes. However, high-quality QDs are typically prepared in organic solvents, and the transfer of QDs to an aqueous phase is needed to create the desired QD composites. Photostability of the transferred QDs—both the steady-state and photo-induced dynamic properties—is essential for studying the processes in the composites and for their applications. We present a detailed study of the photostability of aqueous CdxSeyZn1–xS1–y gradient core–shell QDs obtained by various approaches using linker exchange and surfactant encapsulation. Beside the steady-state photoluminescence (PL) emission stability, we also study changes in the PL decay. From the variety of the studied samples, the water-soluble QDs encapsulated by a double layer of oleic acid show superior properties, that is, stable PL emission and PL decay under continuous light or pulsed-laser light irradiation. We demonstrate that the double-layer encapsulation of QDs can be used to create QDs–metal nanoparticle composites.

# Photostability of the Oleic Acid-Encapsulated Water-Soluble CdxSeyZn1–xS1–y Gradient Core–Shell Quantum Dots\_2017

Polarization resolved fluorescence from single molecules was measured from rhodamine 6G (R6G), sulforhodamine B (SRB), Oregon Green 514 (ORG), and didodecyl-3,3,3‘,3‘-tetramethylindocarbocyanine (DilC12) embedded in silica sol−gel thin films in contact with water and ethanol. Positively charged R6G was found to be firmly immobilized, regardless of the solvent medium. Despite its net negative charge, zwitterionic SRB was found mostly immobilized in both solvent media. The immobilization of SRB was attributed to a delicate balance of Coulombic interaction, hydrogen bonding, and molecular imprinting effect. While R6G showed a significant decrease in photostability in a solvent medium because of enhanced solvent interactions, hydrogen bonding appeared to effectively retard the molecular motions of solvated SRB such that its photostability exceeded those in dry films. The mobility of negatively charged ORG was found to be moderately enhanced through repulsion, but Coulombic force was not as influential as hydrophobic interaction, which was responsible for the high mobility found for DiIC12 in dry films. When in water and ethanol, the hydrophobic chains of DiIC12 were pushed by the solvent toward the less polar silica matrix, forcing DiIC12 to the solid−liquid interface and transforming a substantial amount of tumbling DiIC12 into intermediate DiIC12. Since the photostability of DiIC12 is closely related to the dynamics associated with its hydrophobic chains, DiIC12 in both water-covered and ethanol-covered films displayed comparable photostability because of the similar silica environment surrounding the hydrophobic chains.

# Solvent Effect on Mobility and Photostability of Organic Dyes Embedded inside Silica Sol−Gel Thin Films\_2005

The development of robust dyes is a highly important theme for any applications of dyes. Here we present photophysical and electrochemical characterization of a set of robust dyes based on the thienylnaphthalimide unit. The set is comprised of the thienylnaphthalimide derivatives with phenyl- (Ph-), 4-nitrophenyl- (NO2Ph-), and 4-(diphenylamino)phenyl (Ph2NPh-) substituents as exemplars covering electron-withdrawing to electron-donating groups. The fluorescence quantum yields of the Ph-TNI increases as the solvent polarity increases, while that of Ph2NPh-TNI showed the opposite trend. Changes in the rates of nonradiative decay were found to be a major factor for these contrasting behaviors. Cyclic voltammetry showed that the substituent effects were more apparent for the HOMO energies rather than the LUMO energies. Density functional theory calculations showed that the first singlet excited state of these compounds is a 1π,π\* state with a significant charge transfer character. Ph-TNI and Ph2NPh-TNI are much more stable against photodegradation than coumarin and fluorescein dyes.

# Photophysical and Electrochemical Properties of Thienylnaphthalimide Dyes with Excellent Photostability\_2014

Near-infrared (NIR) light harvesting has enormous importance for different potential applications in the modern era of research. Some NIR cyanine dyes such as IR820 have achieved great success in energy harvesting and cancer therapy. However, their action is limited for low photostability, considerable thermal degradation, short circulation times, and nonspecific biodistribution. Our present study is an attempt to overcome such limitations by attaching a model cyanine dye IR820 with ZnO nanoparticles. We prepared an IR820-ZnO nanohybrid and characterized it using microscopic and optical spectroscopic tools. Thermogravimetric analysis depicted greater thermal stability of the IR820-ZnO nanohybrid compared to free dye. We explored the enhancement in the photostability of IR820 upon nanohybrid formation. We detected generation of photoinduced reactive oxygen species (ROS) such as superoxide, singlet oxygen, and so forth using appropriate molecular probes. The formation of IR820-ZnO nanohybrid reduced production of photoinduced singlet oxygen. However, it revealed an alternative trend in overall ROS formation (increases total ROS) under red light illumination. To correlate the enhanced photostability of IR820 on the ZnO surface, we explored excited-state dynamical processes at the interface in nanohybrids. We illustrated the photoinduced excited-state electron-transfer process from the lowest unoccupied molecular orbital of IR820 to the conduction band of ZnO. This photoelectron-transfer process enhances the production of ROS and decreases the formation of singlet oxygen that altogether leads to improvement in photostability and overall activity. A quencher of singlet oxygen sodium azide (NaN3) was used to further confirm the direct association of singlet oxygen generation with the photostability issue of IR820. Also, ZnO is able to deliver the dye selectively in acidic environment, which suggests its diseased site-specific targeted activity. Our results provide promising improvement for potential use of IR820 through formation of a nanohybrid that could be translated for other NIR cyanine dyes.

# Improvement of Photostability and NIR Activity of Cyanine Dye through Nanohybrid Formation: Key Information from Ultrafast Dynamical Studies\_2019

Abscisic acid (ABA), as a commonly used plant growth regulator, is easy to be degraded and lose its bioactivity under sunshine. To select an eco-friendly and efficient photoprotectant for the improvement of photostability and bioactivity of ABA when exposed to ultraviolet (UV) light, we tested the effects of three biodegradable natural-derived high polymers, sodium lignosulfonates 3A [molecular weight (MW) > 50000, with degree of sulfonation (DS) of 0.48] and NA (20000 < MW < 50000, with DS of 0.7) and calcium lignosulfonate CASA (MW < 20000, with DS of 0.7), on the photodegradation of ABA. Lignosulfonates 3A, NA, and CASA showed significant photostabilizing capability on ABA. Lignosulfonate 3A showed preferable photostabilizing effects on ABA compared to CASA, while NA showed an intermediate effect. That indicated that lignosulfonate with a high MW and low DS had a stronger UV absorption and the hollow aggregate micelles formatted by lignosulfonate protect ABA from UV damage. Approximately 50% more ABA was kept when 280 mg/L ABA aqueous solution was irradiated by UV light for 2 h in the presence of 2000 mg/L lignosulfonate 3A. The bioactivity on wheat (JIMAI 22) seed germination was greatly kept by 3A in comparison to that of ABA alone. The 300 times diluent of 280 mg/L ABA plus 2000 mg/L 3A after 2 h of irradiation showed 20.8, 19.3, and 9.3% more inhibition on shoot growth, root growth, and root numbers of wheat seed, separately, in comparison to ABA diluent alone. We conclude that lignosulfonate 3A was an eco-friendly and efficient agent to keep ABA activity under UV radiation. This research could be used in UV-sensitive and water-soluble agrichemicals and to optimize the application times and dosages of ABA products.

# Lignosulfonate Improves Photostability and Bioactivity of Abscisic Acid under Ultraviolet Radiation\_2017

Single-molecule imaging pushes fluorescence microscopy beyond the diffraction limit of traditional microscopy. Such super-resolution imaging, which relies on the detection of bright, stable fluorescent probes to achieve nanometer-scale resolution, is often hindered in biological systems by dim, blinking fluorescent proteins (FPs). Here, we use gold nanorods and single-molecule fluorescence detection to achieve plasmon-enhanced emission from intrinsically fluorescent proteins. We measure a doubled photon emission rate from the red FP mCherry and detect three times more photons before photobleaching from the photoactivatable FP PAmCherry. We further explore the effect of near-field nanorod interactions on the yellow FP mCitrine, for which the observed emission enhancements cannot overcome measurable quenching. Overall, our work indicates that plasmonic particles improve both the brightness and photostability of FPs and extends the applications of plasmon-enhanced fluorescence to the arena of biological imaging. Furthermore, because gold nanorods are nontoxic, they are promising extracellular imaging substrates for enhancing emission from FP-labeled membrane-bound proteins in live cells.

# Plasmon-Enhanced Brightness and Photostability from Single Fluorescent Proteins Coupled to Gold Nanorods\_2014

Photostability measurements were made on host–guest thin films containing nonlinear optical chromophores with an indoline donor and amorphous polycarbonate. We find that the indoline-based chromophores are nearly 10 times more photostable than an analogous compound previously studied and which has a dihydopyridine donor. There is an enhancement of the photostability with increasing chromophore concentration and conjugation length. This can be attributed to a reduction in the average separation between the chromophores and excited state singlet energy transfer to adjacent chromophores followed by eventual nonradiative decay. This leads to a reduction in the singlet oxygen generation rate as the chromophore concentration or conjugation length is increased.

# Effects of Chromophore Conjugation Length and Concentration on the Photostability of Indoline-Based Nonlinear Optical Chromophore/Polymer Films\_2015

The synthesis of epitaxially grown, wurtzite CdSe/CdS core/shell nanocrystals is reported. Shells of up to three monolayers in thickness were grown on cores ranging in diameter from 23 to 39 Å. Shell growth was controllable to within a tenth of a monolayer and was consistently accompanied by a red shift of the absorption spectrum, an increase of the room temperature photoluminescence quantum yield (up to at least 50%), and an increase in the photostability. Shell growth was shown to be uniform and epitaxial by the use of X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), and optical spectroscopy. The experimental results indicate that in the excited state the hole is confined to the core and the electron is delocalized throughout the entire structure. The photostability can be explained by the confinement of the hole, while the delocalization of the electron results in a degree of electronic accessibility that makes these nanocrystals attractive for use in optoelectronic devices.

# Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility\_1997

The electrolyte composition has a significant effect on the performance and stability of cobalt-based, dye-sensitized solar cells (DSSCs). The stability of DSSCs incorporating Co(II/III) tris(bipyridine) redox mediator has been investigated over 1000 h under full solar irradiation (with UV cutoff) at a temperature of 60 °C, the main focus being on monitoring the photovoltaic performance of the device and analyzing the internal charge-transfer dynamics in the presence of different cation coadditives (preferably added as tetracyanoborate salts). A clear cation-dependence is shown, not only of the early light-induced performance but also of the long-term photostability of the photovoltage of the device. These light-induced changes, which are attributed to the promotion of electron injection and less electron recombination loss, by transient spectral and electrochemical studies at the TiO2/dye/electrolyte interface, indicate that the main cation effects involve the TiO2 surface electric field and energy-state distribution. By examining the stability of adsorbed and solvated dye during aging, it has been found that the dye photodegradation is probably responsible for the decline in the photovoltage and that this is extremely dependent on the nature of the cation coadditives in the electrolyte. It is therefore suggested that optimization of the electrolyte cation composition is essential for improving the stability of cobalt-based DSSCs.

# Cation-Dependent Photostability of Co(II/III)-Mediated Dye-Sensitized Solar Cells\_2015

The mobility and photostability of single rhodamine 6G (R6G) molecules encapsulated in organosilane modified silica alcogel films were used to examine how postsynthesis grafting alters guest−host interactions. While physical confinement remains the major factor that controls mobility in modified alcogels, both R6G mobility and photostability register discernible changes after surface charges are respectively reversed and neutralized by aminopropyltrimethoxysilane (APTS) and methyltriethoxysilane (MTES) grafting to weaken R6G/silica attraction on pore surfaces. Among the two methods, the change in R6G photostability was found to be more sensitive to surface grafting, which is more capable of inducing localized dynamic motions than full scale molecular rotation under the stringent physical confinement inside alcogel films. In addition, silica films modified by 0.4% APTS is as efficient as that by pure MTES in lowering R6G photostability, suggesting that surface charge reversal is more effective than charge neutralization in disrupting R6G/silica attraction. Collectively, our results demonstrate that single-molecule mobility and photostability can be used to monitor the extent of grafting reaction underneath a film surface and complement other surface characterization techniques that are only sensitive to modifications made on a film surface.

# Probing the Effect of Post-Synthesis Grafting on Guest−Host Interactions in Sol−Gel Silica with Single-Molecule Mobility and Photostability\_2009

Two formulation concentrates of the insecticide, tebufenozide, [Mimic®, also known as RH-5992, N'-t-butyl-N'-(3,5-dimethylbenzoyl)-N-(4-ethylbenzoyl) hydrazine], an aqueous flowable (2F) and an emulsion-suspension (ES), were diluted with water and sprayed onto balsam fir branch tips at 140 to 150 g of active ingredient (AI) in 4.0 to 5.0 L/ha. Simulated rainfall was applied onto treated branch tips after different ageing periods of deposits. Foliar washoff of RH-5992 was assessed after application of different amounts of rain. A direct relationship existed between the amount of rainfall and AI washoff. The larger the rain droplet size, the greater the washoff. Longer rain-free periods made the deposits more resistant to rain. Regardless of the amount of rainfall, rain droplet size and ageing period, foliar deposits of the 2F mixture were washed off more than those of the ES mixture.  
Another set of branch tips was exposed to simulated sunlight at two different radiation-free periods, and the emission-intensity spectra were measured. The amount of AI disappeared from foliage after exposure to radiation was measured. A direct relationship existed between radiation intensity and AI disappearance from foliage. The longer the duration of exposure, the greater the disappearance. Unlike the rain-washing, the ageing of foliar deposits had little influence on photo-induced disappearance of the AI. Regardless of the amount and intensity of radiation, and radiation-free period, AI deposits of the ES mixture disappeared more than those of the 2F mixture.

# Photostability and Rainfastness of Tebufenozide Deposits on Fir Foliage\_1995

With the purpose of enhancing the biopharmaceutical properties of the furosemide, a pharmaceutical salt was obtained and characterized by combining the drug and triethanolamine. The solid system was prepared using different techniques such as kneading, grinding, and slow evaporation. It was characterizated by X-ray powder diffraction, solid-state nuclear magnetic resonance, infrared and Raman spectroscopy, thermal analysis, and scanning electron microscopy. The results showed that the same pharmaceutical compound in solid state was obtained through the different preparation techniques. The crystalline structure was fully elucidated by single-crystal X-ray diffraction. The salt formation was confirmed by two-dimensional nuclear magnetic resonance experiments, which revealed the transference of the OH proton of the drug to triethanolamine. Besides, the solubility studies demonstrated an increase in the drug solubility attributed not only to a pH change but also to a soluble salt formation in solution. In addition, the combination of the drug with triethanolamine produces an enhancement of the chemical photostability, whereas the physical photostability and the hygroscopicity status were not modified. Finally, this new solid form of furosemide constitutes an interesting strategy to improve the biopharmaceutical properties and stability of furosemide, with potential application in pharmaceutical formulations.

# Furosemide:Triethanolamine Salt as a Strategy To Improve the Biopharmaceutical Properties and Photostability of the Drug\_2019

UV light can induce chemical reactions in nucleic acids and thereby damage the genetic code. Like all of the five primary nucleobases, the isolated RNA base uracil exhibits ultrafast, nonradiative relaxation after photoexcitation, which helps to avoid photodamage most of the time. Nevertheless, within RNA and DNA strands, commonly occurring photolesions have been reported and are often ascribed to long-lived and delocalized excited states. Our quantum dynamical study now shows that excited-state longevity can also occur on a single nucleobase, without the need for delocalization. We include the effects of an atomistic RNA surrounding in wave packet simulations and explore the photorelaxation of uracil in its native biological environment. This reveals that steric hindrance through embedding in an RNA strand can inhibit the ultrafast relaxation mechanism of uracil, promoting excited-state longevity and potential photodamage. This process is nearly independent from the specific combination of neighboring bases.

# RNA Environment Is Responsible for Decreased Photostability of Uracil\_2018

The effects of supramolecular encapsulation on the photophysics and photostability of a highly fluorescent dimeric derivative of 2,6-diacetoxy-9,10-bis(arylethynyl)anthracene (G2) were investigated by single-molecule fluorescence spectroscopy (SMFS). The fluorescence properties of free-G2 and its self-assembled boronic ester encapsulation complex, G2@(Cap)2, were compared in solution and a glassy polymer film. The fluorescence spectral characteristics and theoretical calculations suggest that the environment affects the excited-state conformation and subsequent fluorescence emission of G2@(Cap)2. In particular, in the liquid and polymer environments, G2@(Cap)2 emits a fluorescence photon in the planar and twist conformation, respectively, whereas the fluorescence-emitting conformation of free-G2 is planar in both environments. The luminous conformation differences between free-G2 and G2@(Cap)2 in polymer are reflected in the intersystem crossing (ISC) parameters (the ISC quantum yield and triplet lifetime), as determined by fluorescence autocorrelation analysis. The photobleaching yield revealed a 3-fold enhancement in the photostability of encapsulated G2 (relative to free-G2). Under the SMFS measurement conditions, the photostability of the encapsulation complex was independent of the guest’s photostability and appeared to be dominated by the thermal stability of the Cap host molecule.

# Effects of Supramolecular Encapsulation on Photophysics and Photostability of a 9,10-Bis(arylethynyl)anthracene-Based Chromophore Revealed by Single-Molecule Fluorescence Spectroscopy\_2016

Application monitors are used to determine the accuracy and precision of pesticide applications made for terrestrial field dissipation studies. Our results show that the photostabilities of two fungicides were affected by the type of paper used as the application monitor and by pesticide formulation. In side-by-side comparisons using an emulsifiable concentrate (EC) formulation, rapid photodegradation of both fungicides occurred when applied to white ∝-cellulose paper. Only 10 to 35% of the applied 14C-fungicides remained as parent after 15-min irradiation in a Suntest photolysis chamber. Dark controls exhibited no losses or degradation under study conditions. In contrast, greater than 85% of the compounds remained as parent when applied to brown Kraft paper. These effects were attributed, in part, to enhanced scattering of light by the white background of the ∝-cellulose paper. When applied as a suspension concentrate (SC) formulation, both fungicides were stable to photolysis on ∝-cellulose and Kraft papers. Differences between these formulations were attributed to either the presence of a photosensitizing agent in the EC and/or increased photostability of the active ingredients in the SC solid phase.

# Photostability of Two Fungicides on Spray Application Monitors: Effect of Paper and Formulation Type\_2002

We have investigated the impact of residual additives such as diiodooctane (DIO) and octanedithiol (ODT) on the photostability of state of the art P3HT:PCBM active layers. A series of active layers prepared with and without additives as well as neat additives were submitted to light irradiation in ambient air and analyzed by UV–vis and IR spectroscopy. We show not only that residues are sensitive to the combined action of light and oxygen but also that their presence can dramatically impact the polymer blend stability. DIO molecules are highly sensitive to light and can directly saturate the polymer conjugated backbone or be trapped by the fullerene moieties. ODT molecules can be photooxidized and may accelerate the intrinsic photooxidation of the active layer. Another important result is that the additives’ impact is directly linked to the presence of a top layer above the active layer. The confinement makes that additives react within the active layer, and thus accelerate its photodegradation, rather than decomposing in the gas phase (irradiation without top layer). Thus, a light-soaking step before top layer deposition could allow a clean removing of additives without affecting the optimized morphology and polymer blend stability. This process would be easily adaptable to industrial scale production.

# The Crucial Role of Confined Residual Additives on the Photostability of P3HT:PCBM Active Layers\_2015

A series of DyxEr(1–x)-polyoxometalates (POMs) were successfully synthesized and characterized well by various physicochemical analysis. The structurally isolated compounds exhibit three characteristic emissions at 480 nm (blue, 4F9/2 → 6H15/2 transition), 573 nm (yellow, 4F9/2 → 6H13/2 transition), and 663 nm (red, 4F9/2 → 6H11/2 transition) whose luminescent color coordinates appear in the near-white area in the CIE 1931 chromaticity diagram. Time-resolved emission spectroscopy was used in DyxEr(1–x)-POM to further authenticate energy transfer from the photoexcitation O → M ligand to the metal charge-transfer state of phosphotungstate components to active Dy3+/Er3+ ions and energy transfer between Dy3+ ion and Er3+ ion via intramolecular energy transitions. The relative emission intensity of ∼32%, ∼53%, and ∼85% for Dy-POM, Dy0.9Er0.1-POM, and Dy0.8Er0.2-POM respectively, were obtained under 300 min of UV irradiation, which indicates better photostability of Dy0.8Er0.2-POM. Furthermore, DyxEr(1–x)-POM samples can emit macroscopic white light under blue irradiation.

# Enhanced Photostability Luminescent Properties of Er3+-Doped Near-White-Emitting DyxEr(1–x)-POM Derivatives\_2018

Solvent additives such as diiodooctane (DIO) are becoming ubiquitous in processing high performance organic photovoltaic (OPV) active layers. Here, we investigate the effects of DIO on the long-term stability of the active layer by studying the photodegradation under ambient white light illumination of the polymer PTB7-Th in pure polymer thin films and in blend films with PC71BM. Using X-ray fluorescence, we directly detect iodine in the active layer films, indicating the presence of residual DIO after casting from solution. Additionally, we show that this residual DIO dramatically decreases the photostability of the active layer. Structural changes in the films upon illumination are probed with grazing-incidence wide-angle X-ray scattering (GIWAXS). FTIR spectroscopy is used to monitor chemical changes in the polymer structure during irradiation in the presence of DIO. Furthermore, we demonstrate that film treatment either with high vacuum (10–8 Torr) for 60 min or with a high-temperature thermal anneal at 175 °C for 30 min removes residual DIO from the film and delays photodegradation. Therefore, when processing polymer solar cells with DIO-containing solutions, it is imperative to remove any trace amounts of DIO from deposited films.

# Removal of Residual Diiodooctane Improves Photostability of High-Performance Organic Solar Cell Polymers\_2016

A two-step synthesis to prepare tricoordinate organoboron compounds bearing three different aryl groups has been developed. After the first aryl substitution to an aryl boronic ester took place, the intermediate species, that is, bis(diarylborinate) species, was isolated as an air- and moisture-stable solid, which allowed the second aryl substitution to carry out in a selective manner. Subsequently, a series of unsymmetrical triarylboranes possessing a sterically bulky aryl group, triarylamine moiety, and para-functionalized phenyl ring was synthesized. Not only did these triarylboranes exhibit remarkable solvent-dependent fluorescence as expected for donor−π–acceptor (D−π–A) systems, they were also accompanied by profound persistence against photoirradiation especially for that bearing a 1,3,5-tri-tert-butylphenyl ring. This survey exemplifies that sufficient electronic and steric modification is key to construct photostable D−π–A type triarylborane-based fluorophores.

# Donor−π–Acceptor Type Unsymmetrical Triarylborane-Based Fluorophores: Synthesis, Fluorescence Properties, and Photostability\_2018

CdS/g-C3N4 core/shell nanowires with different g-C3N4 contents were fabricated by a combined solvothermal and chemisorption method and characterized by X-ray powder diffraction, scanning electronic microscopy, transmission electron microscopy, and UV–vis diffuse reflection spectroscopy. The photocatalytic hydrogen-production activities of these samples were evaluated using Na2S and Na2SO3 as sacrificial reagents in water under visible-light illumination (λ ≥ 420 nm). The results show that after a spontaneous adsorption process g-C3N4 is successfully coated on CdS nanowires with intimate contact and can significantly improve the photocatalytic hydrogen-production rate of CdS nanowires, which reaches an optimal value of up to 4152 μmol h–1 g–1 at the g-C3N4 content of 2 wt %. More importantly, g-C3N4 coating can substantially reinforce the photostability of CdS nanowires even in a nonsacrificial system. The synergic effect between g-C3N4 and CdS, which can effectively accelerate the charge separation and transfer corrosive holes from CdS to robust C3N4, was proposed to be responsible for the enhancement of the photocatalytic activity and photostability. The possible conditions necessary for the synergic effect to work in a CdS/g-C3N4 core/shell configuration is also discussed.

# Efficient Visible-Light Photocatalytic Hydrogen Evolution and Enhanced Photostability of Core/Shell CdS/g-C3N4 Nanowires\_2013

Chalcogenide nanocrystals or quantum dots (QDs) such as CdSe and PbSe have great potential as absorbers for QD-sensitized solar cells, but their practical utility is limited by fast degradation when exposed to ambient environments. Here we present results showing that small organic molecules acting as hole-accepting ligands can be very effective in reducing photooxidation of CdSe QDs. The aromatic amine, 4-dimethylaminothiophenol (DMATP), is shown to be especially effective in enhancing stability of CdSe QDs when illuminated in air or in aqueous environments. Using photoluminescence and density functional theory (DFT) calculations, we show that the enhanced stability results from hole transfer from the QD to the ligand and delocalization of the resulting positive charge on the aromatic ring and amino group instead of the sulfur atom that links the molecule to the CdSe.

# Influence of Hole-Sequestering Ligands on the Photostability of CdSe Quantum Dots\_2012

Azobenzene materials provide an effective way for liquid crystal (LC) alignment besides traditional rubbing technology. A strong relationship between relative humidity (RH) and the photoalignment quality of hydrophilic azobenzene dye brilliant yellow (BY) has been investigated. Good photoalignment quality can only be ensured at about 40% RH or below. On the other hand, the photostability of the alignment layer is also influenced dramatically by RH. The rewritability can be guaranteed at extremely low RH (≤10%). It is gradually lost with increasing RH, and the alignment layer becomes photostable against further light exposure when at 40% RH or above. Therefore, the BY photoalignment layer can be tuned from rewritable to photostable by simply adjusting RH, and thus multistep photopatterned alignments can be obtained and reserved based on this method. Similar properties are also expected for other hydrophilic azobenzene photoalignment materials, where the specific RH values may vary correspondingly. The reason is due to the strong intermolecular interaction and J-aggregate formation of BY molecules with water insertion. Moreover, the lyotropic LC formed by J-aggregated BY molecules in aqueous solution is reported here.

# High Photoinduced Ordering and Controllable Photostability of Hydrophilic Azobenzene Material Based on Relative Humidity\_2018

Little is known about the stability of nitro-polycyclic aromatic hydrocarbons (NPAH) on atmospheric aerosols. In this study, the photostability of particle-associated NPAH was investigated under natural sunlight. Deuterated and native NPAH along with diesel exhaust or wood smoke particles were added to a 190-m3 outdoor smog chamber and permitted to age under sunlight in cold and warm temperatures. Ozone (O3), nitrogen oxides (NOx), and volatile hydrocarbons in the gas phase were monitored. A sampling train consisting of an annular denuder filter plus another denuder was used for the collection of gas- and particle-phase PAH and NPAH. Rapid degradation of deuterated and native NPAH was observed in sunlight, over a temperature range of −19 to +38 °C. Deuterated 1-nitropyrene (d9-1NP) displayed the same behavior as native 1-nitropyrene (1NP), which indicated that it was reasonable to use deuterated NPAH as substitutes for native NPAH. The photolysis rate of NPAH was referenced to the NO2 photolysis rate in order to relate the observed decay of NPAH to the changing solar radiation.To model the decay of NPAH on diesel particles, an average rate constant of kNPAH = (0.04 ± 0.01) × kNO2 was used for nitropyrenes (NPs), and a average rate of kNPAH = (0.025 ± 0.005) × kNO2 was needed to model the behavior of nitrofluoranthenes (NFs). A higher rate, kNPAH = (0.050 ± 0.005) × kNO2, was needed to model the decay of NFs and NPs decay on wood smoke. A photolysis rate of NO2 (kNO2 = 8.3 × 10-3 s-1) at noon on June 15, 1994, gave half-lives of 0.8 h for 1NP and 2-nitropyrene (2NP) and 1.2 h for 2-nitrofluoranthene (2NF), d9-3-, and d9-8-nitrofluoranthene (d9-3NF and d9-8NF) on diesel soot particles. The half-life was 0.5 h for d9-1NP, d9-3NF, and d9-8NF on wood soot particles. These results showed that photodecay was the main loss pathway for NPAH on diesel soot and wood smoke and that photodecomposition of NPAH was dependent on the solar radiation and the chemical and physical properties of the substrates. The effect of temperature was not significant.

# Photostability of Nitro-Polycyclic Aromatic Hydrocarbons on Combustion Soot Particles in Sunlight\_1996

Intercalation of perylenediimide dye into a host layer of layered double hydroxide (LDH) by the anion-exchange method is studied. N,N′-Bis(4-benzosulfonic acid)perylene-3,4,9,10-tetracarboxylbisimide disodium salt (PRSA) has been synthesized and intercalated into the perchlorate form of ZnAl-, CoAl-, and NiAl−LDH. LDH composite with well-defined morphology has been prepared. XRPD and FT-IR investigation show successful intercalation of PRSA, and the interlayer distances are 32.5 Å for ZnAl−LDH−PRSA, 30.0 Å for CoAl−LDH−PRSA, and 31.2 Å for NiAl−LDH−PRSA. These values support the presence of monolayer arrangement of intercalated PRSA molecules in the composite and also indicate vertical orientation of PRSA molecules with the basal plane of LDH. Photophysical properties of these intercalated composites have been measured with UV−vis spectroscopy, photoluminescence spectroscopy, and confocal laser scanning microscopy. The results indicate that the PRSA molecules are stacked in J-type aggregation in the interlayer region. Intercalated PRSA molecules show enhanced thermal and photophysical stabilities.

# Intercalation of Perylenediimide Dye into LDH Clays: Enhancement of Photostability\_2010

Carbohydrates are essential building blocks of life that assume a multitude of biological functions in all living organisms found on Earth. It was recently reported that ribose was identified in UV-irradiated interstellar ice analogs, which suggests that it can be found on comets and that it may have been transported to Earth via the impact of comets. Herein, we present computational results obtained with multiconfigurational ab initio quantum-chemical methods showing that various photochemical processes for radiationless deactivation are available for photoexcited ribose. These processes are driven by nσ\* states and involve either O–H- or endocyclic or exocyclic C–O-bond elongation whereby a conical intersection with the electronic ground state becomes accessible. The local topography of the potential-energy surfaces around these conical intersections suggests that these intersections mediate efficient radiationless deactivation and favor regeneration of the initially photoexcited ground-state reactant. These findings indicate that ribose found in interstellar space can be expected to be highly photostable upon irradiation with UV starlight, which could be of relevance in the field of astrobiology.

# Conical-Intersection Topographies Suggest That Ribose Exhibits Enhanced UV Photostability\_2016

Carboxylic acid moieties are used to anchor organic dyes to TiO2 in many applications; therefore, their structure, distribution on the surface, and thermal and photochemical stability are extremely important. Herein, we investigate the thermal and photochemistry of benzoic acid monolayers on TiO2. Benzoic acid deprotonates to form benzoate monomers on the TiO2 surface, and thermally decomposes to benzene and CO. Titanium interstitials migrate to the surface and react with oxygen atoms from the benzoate molecules to form new TiOx islands. A combination of X-ray photoelectron spectroscopy and scanning tunneling microscopy shows that the benzoate layer on TiO2 is stable under UV illumination for several hours. The stability of benzoate under illumination is in contrast to the photochemical instability of other small carboxylic acid containing molecules on TiO2 and demonstrates the importance of substituents on the stability of the molecular layer.

# Photostability and Thermal Decomposition of Benzoic Acid on TiO2\_2012

Single-molecule fluorescence microscopy at an air–solid interface severely suffers from photobleaching. In this study, we evaluated using a triplet-state quencher cyclooctatetraene (COT) group to enhance the photostability of cy5-attached molecular machines. For single-dye-modified nanocars, the photobleaching lifetime of the dye was extended by 2.1 times after the attachment of the COT group. For two-COT-two-dye-attached unimolecular submersible nanomachine (USN) molecules, both one-step and two-step photobleaching of the dyes were observed, similar to those cy5-USNs without COT protection. The fraction of one-step photobleaching events was nearly a constant under different laser powers, indicating that one-step photobleaching is a single-photon process and that the product of the first photobleaching event destroys the second dye. The COT-cy5-USNs showed a larger fraction of two-step photobleaching events as compared to cy5-USNs, indicating that the COT group provides further protection for the second dye from the oxidative product generated in the first dye photobleaching process. Overall, the protected, doubly labeled COT-cy5-USN molecules have a total photobleaching lifetime extended by 2.4 times over unprotected cy5-USN molecules or by 3.3 times over unprotected, single cy5-labeled molecules. This study shows the potentials and the limits of using triplet quencher COT to protect fluorescent dyes at the air–glass interface.

# Enhancing Photostability of Fluorescent Dye-Attached Molecular Machines at Air–Glass Interface Using Cyclooctatetraene\_2019

A new route for the nonradiative decay of photoexcited, H-bonded, nitrogen-containing, heterocyclic dimers is offered and exemplified by a study of the pyrazole dimer. In some of these systems the N(3s) Rydberg state is the lowest excited singlet state. This state is formed by direct light absorption or by nonradiative transition from the allowed ππ\* state. An isomer of this Rydberg state is formed by H atom transfer to the other component of the dimer. The newly formed H-bonded radical pair is composed of two radicals (a H-adduct of pyrazole, a heterocyclic analogue of the NH4 radical) and the pyrazolium π-radical. It is calculated to have a shallow local minimum and is the lowest point on the PES of the H-pyrazole/pyrazolium radical pair. This species can cross back to the ground state of the original dimer through a relatively small energy gap and compete with the H-atom loss channel, known for the monomer. In both Rydberg dimers, an electron occupies a Rydberg orbital centered mostly on one of the two components of the dimer. This Rydberg Center Shift (RCS) mechanism, proposed earlier (Zilberg, S.; Kahan, A.; Haas, Y. Phys. Chem. Chem. Phys.2012, 14, 8836), leads to deactivation of the electronically excited dimer while keeping it intact. It, thus, may explain the high photostability of the pyrazole dimer as well as other heterocyclic dimers.

# Role of Rydberg States in the Photostability of Heterocyclic Dimers: The Case of Pyrazole Dimer\_2012

A series of electronically active viologen dications (RV) with tunable substituent groups were utilized to hybridize with [Ge4S10]4– (T2 cluster) to form the hybrids of T2@RV. These hybrids exhibited variable supermolecular assembly formation, tunable optical absorption properties, and different photoelectric response under the influence of different RV dications. Raman testing and time-dependent photocurrent response indicated that the photosensitivity and photostability of T2@RV could be integrated while choosing suitable RV dications. Current research provides a general method to build a tunable hybrid system based on crystalline metal chalcogenide compounds through the replacement of photoinactive cationic organic templates with photoactive ones with different substituent groups.

# Substituent-Modulated Assembly Formation: An Approach to Enhancing the Photostability of Photoelectric-Sensitive Chalcogenide-Based Ion-Pair Hybrids\_2017

On the basis of an extensive ab initio electronic structure study of the ground and excited-state potential energy surfaces of the naphthalene radical cation (N•+), we propose a mechanism for its ultrafast nonradiative relaxation from the second excited state (D2) down to the ground state (D0), which could explain the experimentally observed photostability [Zhao, L.; Lian, R.; Shkrob I. A.; Crowell, R. A.; Pommeret, S.; Chronister, E. L.; Liu, A. D.; Trifunac, A. D. J. Phys. Chem. A., 2004, 108, 25]. The proposed photophysical relaxation pathway involves internal conversion from the D2 state down to the D0 state via two consecutive, accessible, sloped conical intersections (CIs). The two crossings, D0/D1 and D1/D2, are characterized at the complete active space self-consistent field (CASSCF) level. At this level of theory, the D0/D1 crossing is energetically readily accessible, while the D1/D2 CI appears too high in energy to be involved in internal conversion. However, the inclusion of dynamic correlation effects, via single point CASPT2 calculations including excitations out of the valence π- and σ-orbitals, lowers the D0 and D2 state energies with respect to D1. Extrapolations at the CASPT2 level predict that the D1/D2 crossing is then significantly lower in energy than with CASSCF indicating that with a higher-level treatment of dynamic correlation it may be energetically accessible following vertical excitation to D2. N•+ is proposed as one of the species contributing to a series of diffuse infrared absorption bands originating from interstellar clouds. Understanding the mechanism for photostability in the gas phase, therefore, has important consequences for astrophysics.

# Photostability Via Sloped Conical Intersections:  A Computational Study of the Excited States of the Naphthalene Radical Cation\_2006

The incorporation of colloidal quantum dots (QDs) into ionic crystals of various salts (NaCl, KCl, KBr, etc.) is demonstrated. The resulting mixed crystals of various shapes and beautiful colors preserve the strong luminescence of the incorporated QDs. Moreover, the ionic salts appear to be very tight matrices, ensuring the protection of the QDs from the environment and as a result providing them with extraordinary high photo- and chemical stability. A prototype of a white light-emitting diode (WLED) with a color conversion layer consisting of this kind of mixed crystals is demonstrated. These materials may also find applications in nonlinear optics and as luminescence standards.

# Colloidal Nanocrystals Embedded in Macrocrystals: Robustness, Photostability, and Color Purity\_2012

For fluorescence-based single-molecule studies, photobleaching of the dye reporter often limits the time window over which individual molecules can be followed. As such, many strategies, for example, using a cocktail of chemical reagents, have been developed to decrease the rate of photobleaching. Herein, we introduce a new and highly effective method to enhance the photostability of one of the commonly used fluorescent dyes, rhodamine 6G (R6G). We show that micrometer-sized polydimethylsiloxane (PDMS) wells, when the PDMS surface is properly treated, not only provide a confined environment for single-molecule detection but can also significantly increase the survival time of individual R6G molecules before photobleaching. Moreover, our results suggest, consistent with several previous studies, that R6G photobleaching involves a radical state.

# Simple Method to Enhance the Photostability of the Fluorescence Reporter R6G for Prolonged Single-Molecule Studies\_2013

The most efficient solar energy utilization is achieved in natural photosynthesis through elaborate cell membrane with many types of molecules ingeniously transferring photogenerated electrons to reactants in a manner similar to the so-called Z-scheme mechanism. However, artificial photosynthetic systems based on semiconductor nanoparticles are inevitably accompanied by undesired non-Z-scheme electron transfer and back reactions, which adversely affect the photoactivity and photostability of the systems. Herein, we report on a novel Z-scheme system with an electrochemically converted graphene (GR) film as the electron mediator interlayer contacted with both TiO2 nanotube (TNT) array and CdS quantum dots (CdS QDs) on two sides. The obtained TiO2 nanotube array–graphene–CdS quantum dots (TNT-GR-CdS) composite film shows higher photoelectric response and photocatalytic activities than other bare TNT, TNT-CdS, TNT-GR, and TNT-CdS-GR. Moreover, compared to TNT-CdS, the activity stability is significantly improved, and the residual amount of Cd element in reaction solution is reduced ∼8 times over TNT-GR-CdS. Various measurements of photoelectrochemistry and radicals reveal that the enhanced photoactivity and photostabilities of TNT-GR-CdS are due to the efficient spatial separation of the photogenerated electron–hole pairs and the restricted photocorrosion of CdS via an efficient Z-scheme mechanism under simulated sunlight.

# TiO2 Nanotube Array—Graphene—CdS Quantum Dots Composite Film in Z-Scheme with Enhanced Photoactivity and Photostability\_2014

Intercalation of 2-hydroxy-5-(4-sulfophenyl azo)-benzoate disodium salt into ZnAl−NO3 layered double hydroxide was carried out in an effort to improve its thermostability and photostability. After intercalation, the powder X-ray diffraction pattern showed that the interlayer distance of the LDH increased from 0.90 to 1.54 nm, suggesting that the HSAB anions are arranged in the interlayer galleries of ZnAl−HSAB−LDH as a tilted monolayer of dianions. Infrared spectra and TG-DTA curves revealed the presence of a complex system of supramolecular host−guest interactions between LDH layers and HSAB anions. The thermostability of HSAB and ZnAl−HSAB−LDH was investigated by TG-DTA and UV−vis spectroscopy; it was found that ZnAl−HSAB−LDH was more stable than HSAB at high temperatures. Photostability tests showed that ZnAl−HSAB−LDH exhibited higher stability to UV radiation than either HSAB or a physical mixture of HSAB and ZnAl−NO3−LDH. In their composites with polyethylene, it was also found that ZnAl−HSAB−LDH possesses better thermostability and photostability than HSAB.

# Enhancement of the Thermo- and Photostability of an Anionic Dye by Intercalation in a Zinc−Aluminum Layered Double Hydroxide Host\_2008

The systematic synthesis of five 1-, 3-, 6-, and 8-tetrasubstituted asymmetric pyrenes with electron donor and acceptor moieties is presented, together with an examination of their photophysical properties. Pyrene derivative PA1, containing one formyl and three piperidyl groups, showed bright solvatochromic fluorescence from green (λem = 557 nm, ΦFL = 0.94 in hexane) to red (λem = 648 nm, ΦFL = 0.50 in methanol), suggesting potential applications for PA1 as an environmentally responsive probe. Although the synthesis of simple 1- and 3-disubstituted pyrene derivatives is considered difficult, PA13, with two formyl groups at the 1- and 3-positions and two piperidyl groups at the 6- and 8-positions, could be synthesized successfully. PA13 exhibited less pronounced solvatochromism, but displayed a narrow fluorescent band with high ΦFL in all solvents (ΦFL > 0.75). Moreover, its absorption band displayed an exceptional bathochromic shift compared to the other derivatives (e.g., λabs = 480 and 522 nm in ethanol for PA1 and PA13, respectively), suggesting that such modifications of pyrene may be quite important for the modulation of its energy gap. Additionally, all compounds exhibited exceptionally high photostability, which highlights the advantage of these new dyes and provides new insights on the design of photostable fluorophores.

# 1-, 3-, 6-, and 8-Tetrasubstituted Asymmetric Pyrene Derivatives with Electron Donors and Acceptors: High Photostability and Regioisomer-Specific Photophysical Properties\_2015

Great care has been paid to the biointerface between a bulk material and the biological environment, which plays a key role in the optimized performance of medical devices. In this work, we report a new superhydrophilic adsorbate, called l-cysteine betaine (Cys-b), having branched zwitterionic groups that give rise to surfaces and nanoparticles with enhanced chemical stability, biofouling resistance, and inertness to environmental changes. Cys-b was synthesized from the amphoteric sulfur-containing amino acid, l-cysteine (Cys), by quaternization of its amino group. Gold surfaces modified with Cys-b exhibited prominent repellence against the nonspecific adsorption of proteins, bacteria, and fibroblast cells. In addition, Cys-b existed in zwitterionic form over a wide pH range (i.e., pH 3.4 to 10.8), and showed excellent suppression in photoinduced oxidation on gold substrates. Furthermore, the modification of hollow Ag@Au nanoshells with Cys-b gave rise to nanoparticles with excellent colloidal stability and resistance to coordinative interaction with Cu2+. Taken together, the unique features of Cys-b offer a new nanoscale coating for use in a wide spectrum of applications.

# Bioinspired Zwitterionic Surface Coatings with Robust Photostability and Fouling Resistance\_2015

A class of pyridmylpyrimidine fungicides represented by compound 1 is presented. Synthetic methods for the preparation of these novel compounds and structure-activity relationships are discussed. These compounds show broad spectrum control of plant pathogens with excellent activity on wheat eyespot (Pseudocercosporella herpotrichoides), wheat leaf blotch (Septoria nodorum) and rice blast (Pyricuiaria oryzae). The impact of photolability on the commercial viability of this class of fungicides is highlighted.

# Pyridinylpyrimidine Fungicides: Synthesis, Biological Activity, and Photostability of Conformationally Constrained Derivatives\_1998

# The Effect of Oxidation Products on the Photostability of Polypropylene Films\_1968

Kynurenines are UV filters found in the human ocular lens which protect the retina from radiation damage. We report on ab initio investigations of the photochemistry of the cis and trans conformers of kynurenine and of an intramolecularly hydrogen-bonded conformer of 3-hydroxykynurenine O-β-d-glucoside. We have explored the excited-state reaction paths for several radiationless excited-state deactivation processes in kynurenines. We show that electron-driven proton-transfer processes mediated by an excited state of charge-transfer character exhibit negligible barriers and that the relevant potential-energy profiles are lower in energy than the lowest absorbing ππ\* state. In these proton-transfer processes, a proton moves from one of the amino groups of kynurenine to the keto group. We also report on nonadiabatic trajectory-surface-hopping molecular-dynamics simulations for photoexcited kynurenine. These simulations show that the cis and trans conformers of kynurenine deactivate on a femtosecond-to-picosecond time scale preferably via electron-driven proton transfer from one of the amino groups to the keto group. Cis kynurenine deactivates via a ring-N—H···O═C proton-transfer process. Trans kynurenine tends to undergo trans → cis isomerization before deactivating via the same process. These results suggest that the deactivation process involving the ring-amino group in the cis conformer of kynurenine is the most efficient excited-state deactivation process in kynurenines. The joint electronic-structure calculations and dynamics simulations provide a new level of mechanistic insight into the efficient UV-filtering capacity of kynurenines.

# Mechanisms of Photostability in Kynurenines: A Joint Electronic-Structure and Dynamics Study\_2014

The photostability of semiconductor PbSe nanocrystals (NCs) under different storage conditions and the photoluminescence of PbSe NC films on Si substrates under vacuum and under different atmospheres were investigated. The NCs show a small blue shift in both the emission and absorption spectra when stored in solution. This blue shift is accelerated when the particles are stored in room light compared to when the particles are stored in the dark, which indicates that photooxidation is an important process. The photooxidation process is accelerated by irradiating NC solutions with a 450 W xenon lamp. The photobleaching and appearance of a precipitate are attributed to ligand desorption followed by agglomeration. Reversible O2-induced luminescence quenching was observed on a PbSe NC film on Si substrates, which could be addressed by two mechanisms:  indirect quenching by alteration of PbSe charging and neutralization dynamics or quenching through direct interaction of O2 with the exciton. To improve the photostability of PbSe NCs, PbSe/PbS core/shell NCs using (TOP)S (TOP = trioctylphosphine) and TMS2S (TMS2 = bis(trimethylsilyl)) as sulfur sources were prepared. However, PbSe/PbS core/shell NCs did not show an increased stability in solution upon irradiation with a xenon lamp when compared with PbSe core NCs. Either the PbS shell is not able to confine the charge carriers or there is incomplete shell passivation with the PbSe core, and as a result these core/shell NCs have comparable stability.

# Photostability of Colloidal PbSe and PbSe/PbS Core/Shell Nanocrystals in Solution and in the Solid State\_2006

The photophysics of the pyrene radical cation, a polycyclic aromatic hydrocarbon (PAH) and a possible source of diffuse interstellar bands (DIBs), is investigated by means of hybrid molecular mechanics−valence bond (MMVB) force field and multiconfigurational CASSCF and CASPT2 ab initio methods. Potential energy surfaces of the first three electronic states D0, D1, and D2 are calculated. MMVB geometry optimizations are carried out for the first time on a cationic system; the results show good agreement with CASSCF optimized structures, for minima and conical intersections, and errors in the energy gaps are no larger than those found in our previous studies of neutral systems. The presence of two easily accessible sloped D1/D2 and D0/D1 conical intersections suggests the pyrene radical cation is highly photostable, with ultrafast nonradiative decay back to the initial ground state geometry predicted via a mechanism similar to the one found in the naphthalene radical cation.

# Photostability via Sloped Conical Intersections: A Computational Study of the Pyrene Radical Cation\_2008

In this work, highly photostable and fluorescent coassembled microsheets were fabricated from molecules 1 and 2 for sensitive and selective detection of BTX. We demonstrate that Förster resonance energy transfer (FRET) from nonphotostable 1 to photostable 2 gives rise to the high photostability of 1–2 coassembled microsheets. Furthermore, the combined properties of 1 and 2 components in coassembled microsheets allow distinct responses to BTX and other VOC vapors and thereby yield highly sensitive and selective detection of BTX hydrocarbons via FRET. These findings provide a new approach for the development of photostable fluorescence sensors for hazardous chemicals.

# Highly Selective Detection of Benzene, Toluene, and Xylene Hydrocarbons Using Coassembled Microsheets with Förster Resonance Energy Transfer-Enhanced Photostability\_2018

Hydroxocobalamin is a potential biocompatible source of photogenerated hydroxyl radicals localized in time and space. The photogeneration of hydroxyl radicals is studied using time-resolved spectroscopy and theoretical simulations. Radicals are only generated for wavelengths <350 nm through a mechanism that involves competition between prompt dissociation and internal conversion. Characterization of the lowest-lying singlet potential energy surface provides insight into the photochemistry of hydroxocobalamin and other cobalamin compounds.

# Photostability of Hydroxocobalamin: Ultrafast Excited State Dynamics and Computational Studies\_2015

Despite the burgeoning development and extensive commercialization of sunscreens, challenges remain regarding the biocompatibility and efficacy of commercial sunscreens. Direct exposure to UV filters has given rise to health problems, including the percutaneous penetration and the generation of reactive oxygen species. To address these, we have developed organic UV-filter self-framed microparticles, whereby organic UV-filter molecules self-construct into nanoparticles without any supportive microencapsulation. This approach is unique for its outstanding biocompatibility by reducing the percutaneous penetration of organic UV-filter molecules. Furthermore, the shielding range is extended from the UVB to the entire UV region by the introduction of a physical reflection effect. An in vitro fibroblast culture experiment and the results of in vivo skin protection experiments confirmed their safety. All the experimental results supported the conclusion that sunblock with self-framed microparticles (FSFMPs) has a great potential to become the next generation of UV filters for the UV protection of skin.

# Perspectives on the Next Generation of Sunscreen: Safe, Broadband, and Long-Term Photostability\_2019

In an attempt to develop a photostable and efficient pyrromethene compound for use in liquid dye lasers, three congeners of the commercially available pyrromethene 567 (PM567) laser dye were synthesized and their photophysical properties, lasing efficiencies, and photochemical stabilities were studied. In general the presence of an aryl group at C-8 of the pyrromethene chromophore increased the photostability. One of the congeners possessing a C-8 trimethoxyphenyl moiety showed significantly improved lasing parameters than PM567. Compared to PM567, the photochemical stability of the new dye was 2-fold, while it showed an equivalent lasing efficiency to that of PM567 at a significantly lower concentration. The increased photostability of these new dye molecules could be explained by theoretical calculation on their capacity to generate singlet oxygen (1O2) and probability of reaction with 1O2. Our calculations were in agreement with the experimental results and indicated that a systematic design of new derivatives of pyrromethene chromophore might lead to improved laser dye molecules.

# Design and Development of a New Pyrromethene Dye with Improved Photostability and Lasing Efficiency:  Theoretical Rationalization of Photophysical and Photochemical Properties\_2008

A polyfluorinated cyanine dye has been synthesized and characterized. Compared with the nonfluorinated analogue, the dye exhibits significantly reduced aggregation in aqueous media, enhanced fluorescence quantum yield, greater resistance to photobleaching upon direct irradiation, and reduced reactivity toward singlet oxygen. All of these properties are favorable for use of cyanine dyes as fluorescent labels and point toward fluorination as a general strategy for improving performance in imaging applications.

# Improved Photostability and Fluorescence Properties through Polyfluorination of a Cyanine Dye\_2004

We report on the photostability of monolayer (1L) transition-metal dichalcogenides (TMDCs) in air and in aqueous solutions, as probed using photoluminescence spectroscopy. 1L-WSe2 was readily degraded under continuous irradiation of visible light in aqueous solutions, whereas 1L-MoS2 was relatively stable in both ambient air and aqueous solutions. The stability difference between these two materials was mainly ascribed to the oxidization reaction at the interface of 1L-TMDCs and the O2/H2O redox system induced by both band alignment and photogenerated holes. This interpretation was strongly supported by the observation of the lower degradation rate of 1L-WSe2 in the dark and in degassed water with a lower concentration of dissolved oxygen compared with the degradation rate of 1L-WSe2 in distilled water. Furthermore, the degradation rate was also nearly proportional to the number of photogenerated carriers. The degradation rate under acidic conditions was smaller than that under the basic conditions. The results are attributed to the oxidation/reduction potential of 1L-WSe2 and to the dissolution reaction of degraded species, both of which are strongly pH-dependent.

# Photostability of Monolayer Transition-Metal Dichalcogenides in Ambient Air and Acidic/Basic Aqueous Solutions\_2019

A goal of our work was to design and synthesize novel Mn(II), Co(II), and Cu(II) complexes with rhodamine C (RHC) and rhodamine 640 perchlorate (RHP) to obtain knowledge about the thermal stability of rhodamine itself compared with its complexes. The complexes prepared have the general formulas [M(L)2(H2O)2]·nH2O and [Cu(L)2]·H2O, where (M = Mn(II) or Co(II), L = RHC or RHP, n = 2 or 4). The complexes obtained were characterized using elemental analysis, magnetic measurements, molar conductivity, and infrared and electronic spectra as well as thermal measurements. The results suggested that all the RHC and RHP complexes had a 1:2 molar ratio (metal:L). Both RHC and RHP act as a bidentate chelating ligand through the carboxylic groups. The molar conductance measurements proved that the Mn(II), Co(II), and Cu(II) complexes of RHC and RHP are nonelectrolytes. Kinetic thermodynamic parameters such as E\*, ΔH\*, ΔS\*, and ΔG\* were calculated from differential thermogravimetric curves. The fluorescence and photostability studies were checked for both fluorescence dyes and their complexes.

# Cu(II), Co(II), and Mn(II) Complexes of Rhodamine C and Rhodamine 640 Perchlorate: Synthesis, Spectroscopic, Thermal, Fluorescence, and Photostability Studies\_2011

The effects of oxygen on the photochemical properties of ruthenium(II) complexes in solution and in polymers are reported. In solution, the complex is actually protected from decomposition by the presence of oxygen as a result of deactivation of the complex by oxygen quenching before it can undergo ligand loss by monomolecular dissociation; however, in polymers, the presence of oxygen increases photochemical decomposition. Singlet molecular oxygen, a product of the oxygen quenching process, may attack the ground state complex or triplet oxygen may directly attack the excited state of the complex. Both mechanisms may be involved in the photodestruction of the complex. The role of oxygen in the photodecomposition was examined by monitoring the photochemical decomposition of various complexes of different singlet oxygen reactivity, as well as absorption and mass spectroscopy studies. It is suggested that in polymers, unlike in solutions, the newly formed reactive singlet oxygen is not able to diffuse away from the complex. The singlet oxygen, trapped in close proximity to the metal complex, has an enhanced opportunity to attack it. This cage effect is supported by studies using tris(1,10-phenanthroline)ruthenium(II) in poly(ethylene glycol) of increasing molecular weight to create an increasingly constraining cage around the complex. Increased poly(ethylene glycol) molecular weight leads to increased oxygen attack of the complex, supporting the cage effect.

# Photostability of Luminescent Ruthenium(II) Complexes in Polymers and in Solution\_2003

We report a facile strategy to fabricate a cadmium sulfide–ferrite (CdS–MFe2O4, M = Zn, Co) nanocomposite with differing ferrite content via a two-step hydrothermal method and demonstrate its application as a magnetically recyclable photocatalyst with enhanced visible-light-driven photocatalytic activity and photostability. The photocatalytic activities of as-prepared photocatalysts are evaluated by the degradation of rhodamine B (RhB) and 4-chlorophenol (4-CP) in aqueous solution under visible-light irradiation. Compared with pure CdS, both CdS–ZnFe2O4 and CdS–CoFe2O4 show more broad absorption in the visible-light region, which favors the visible-light utilization for better photocatalytic performance. Moreover, the surface area of cadmium sulfide–ferrite is much higher than that of pure CdS, also resulting in enhanced photocatalytic activity. Furthermore, the synergic effects of CdS and ferrites can reduce the recombination probability of photogenerated electron–hole pairs and enhance the charge separation efficiency, leading to high photocatalytic performance and remarkable inhibited photocorrosion.

# Cadmium Sulfide–Ferrite Nanocomposite as a Magnetically Recyclable Photocatalyst with Enhanced Visible-Light-Driven Photocatalytic Activity and Photostability\_2013

We have studied the multiphoton photodissociation of (C2H2)n and (C2H2)n·Arm clusters in molecular beams. The clusters were prepared in supersonic expansions under various conditions, and the corresponding mean cluster sizes were determined, for which the photodissociation at 193 nm was studied. The measured kinetic energy distributions (KEDs) of the H fragment from acetylene in clusters peak around 0.2 eV, in agreement with the KED from an isolated C2H2 molecule. However, the KEDs from the clusters extend to kinetic energies of over 2 eV, significantly higher than the maximum fragment energies from an isolated molecule of about 1 eV. The photofragment acceleration upon solvation is a rather unusual phenomenon. The analysis based on ab initio calculations suggests the following scenario: (i) At 193 nm, photodissociation of acetylene occurs mostly in the singlet manifold. (ii) The solvent stabilizes the acetylene molecule, preventing it from undergoing hydrogen dissociation and funneling the population into a vibrationally hot ground state. (iii) The excited C2H2 absorbs the next photon and eventually dissociates, yielding the H fragment with a higher kinetic energy corresponding to the first C2H2 excitation. Thus, the H-fragment KED extending to higher energies is a fingerprint of the cage effect and the multiphoton nature of the observed processes. The photon-flux dependence of the KEDs reflects the rate of the vibrational energy flow from the hot ground state of acetylene to the neighboring solvent molecules.

# Solvent-Induced Photostability of Acetylene Molecules in Clusters Probed by Multiphoton Dissociation\_2009

Hybrid graphene–perovskite photodetectors embrace the excellent photoabsorption properties of perovskites and high carrier mobility of graphene in a single device. Here, we demonstrate the integration of halide-ion-exchanged CsPbBrxI3–x nanocrystals (NCs) as a photoabsorber and graphene as a transport layer. The NCs conform to a cubic lattice structure and exhibit an optical band gap of 1.93 eV. The hybrid device attained a maximum responsivity of 1.13 × 104 A/W and specific detectivity of 1.17 × 1011 Jones in low light intensity (∼80 μW/cm2). Specifically, an ultrahigh photoconductive gain of 9.32 × 1010 is attained because of fast hole transit time in the graphene transistor and long recombination lifetime in the perovskite NCs simultaneously. The phototransistor also shows good stability and can maintain ∼95% of the photocurrent under continuous illumination over 5 h and ∼82% under periodic illumination over 37 h. Our results also revealed that the common issue of ion separation and segregated halide domains in mixed halide perovskite NCs do not occur under low light intensities. The intensive degradation of CsPbBrxI3–x NCs is only observed under stronger light excitation (≥55 mW/cm2), reflecting as emission shifts. Our work establishes the use of fully inorganic perovskite NCs as highly stable photodetectors with high responsivity and low power light detection.

# All Inorganic Mixed Halide Perovskite Nanocrystal–Graphene Hybrid Photodetector: From Ultrahigh Gain to Photostability\_2019

Lipid vesicle encapsulation is an efficient approach to transfer quantum dots (QDs) into aqueous solutions, which is important for renewable energy applications and biological imaging. However, little is known about the molecular organization at the interface between a QD and lipid membrane. To address this issue, we investigated the properties of 3.0 nm CdSe QDs encapsulated within phospholipid membranes displaying a range of phase transition temperatures (Tm). Theoretical and experimental results indicate that the QD locally alters membrane structure, and in turn, the physical state (phase) of the membrane controls the optical and chemical properties of the QDs. Using photoluminescence, ICP-MS, optical microscopy, and ligand exchange studies, we found that the Tm of the membrane controls optical and chemical properties of lipid vesicle-embedded QDs. Importantly, QDs encapsulated within gel-phase membranes were ultrastable, providing the most photostable non-core/shell QDs in aqueous solution reported to date. Atomistic molecular dynamics simulations support these observations and indicate that membranes are locally disordered displaying greater disordered organization near the particle–solution interface. Using this asymmetry in membrane organization near the particle, we identify a new approach for site-selective modification of QDs by specifically functionalizing the QD surface facing the outer lipid leaflet to generate gold nanoparticle–QD assemblies programmed by Watson–Crick base-pairing.

# Quantum Dots Encapsulated within Phospholipid Membranes: Phase-Dependent Structure, Photostability, and Site-Selective Functionalization\_2014

The rational design of environmentally sensitive dyes with superior properties is critical for elucidating the fundamental biological processes and understanding the biophysical behavior of cell membranes. In this study, a novel group of fluorene-based push–pull probes was developed for imaging membrane lipids. The design of these fluorogenic conjugates is based on a propioloyl linker to preserve the required spectroscopic features of the core dye. This versatile linker allowed the introduction of a polar deoxyribosyl head, a lipophilic chain, and an amphiphilic/anchoring group to tune the cell membrane binding and internalization. It was found that the deoxyribosyl head favored cell internalization and staining of intracellular membranes, whereas an amphiphilic anchor group ensured specific plasma membrane staining. The optimized fluorene probes presented a set of improvements as compared to commonly used environmentally sensitive membrane probe Laurdan such as red-shifted absorption matching the 405 nm diode laser excitation, a blue-green emission range complementary to the red fluorescent proteins, enhanced brightness and photostability, as well as preserved sensitivity to lipid order, as shown in model membranes and living cells.

# Turn-on Fluorene Push–Pull Probes with High Brightness and Photostability for Visualizing Lipid Order in Biomembranes\_2017

In the present work, 9-anthraceneacetic acid (1) has been selected as a simple, water-compatible derivative of the anthracene chromophore to investigate the photophysical and photochemical behavior upon binding to human and bovine serum albumins (HSA and BSA) and α-acid glycoproteins (HAAG and BAAG). The UV−vis absorption spectrum of 1 exhibited the typical four maxima between 320 and 400 nm, which were slightly red-shifted in the presence of proteins. These minor changes suggested the formation of 1@protein complexes; their stoichiometry (1:1) was determined by means of the corresponding Job plots. As expected, the fluorescence spectrum of 1 in phosphate-buffered saline (PBS) consisted of a structured emission with maxima between 390 and 470 nm. The addition of increasing amounts of HSA resulted in a decrease in the emission intensity. In the presence of BSA, HAAG, or BAAG, the same trend was observed, although the changes were less pronounced. The determination of binding constants was achieved from fluorescence titration, considering one (AAGs) or two (SAs) binding sites. The binding constants (KB) were found to be 2.3 × 106 M−1 (HAAG), 2.4 × 106 M−1 (BAAG), 4.57 × 104/1.45 × 106 M−1 (HSA), and 1.44 × 104/1.20 × 106 M−1 (BSA). Binding within two different sites of SAs was confirmed by displacement experiments using warfarin and ibuprofen as site I and site II probes, respectively. Laser flash photolysis of 1 at λexc = 355 nm in PBS/air gave rise to several transient species; by contrast, in the presence of 1 equiv of proteins, only the triplet excited state was detected. Moreover, the triplet lifetime (τT) monitored at 420 nm lengthened considerably (up to 50-fold) in the protein media. This can be attributed to a slower deactivation of the species inside the protein binding pockets, where an exceptional microenvironment provides protection from attack by a second molecule of 1, oxygen, or other reagents. In agreement with the results from fluorescence titration, the presence of two binding sites in SAs was revealed by two different triplet lifetimes; by contrast, only one τT value was found for HAAG and BAAG. The major, longer-lived component under nonsaturating conditions was assigned to (1@SA)II, while the minor component was assigned to (1@SA)I. Irradiation of 1 at 350 nm in PBS/air led to anthraquinone as a major product. In the presence of proteins, the degree of conversion was markedly lower than in PBS, as revealed by the photodegradation kinetics monitored through the absorbance changes at 367 nm. Thus, a dramatic protection from photooxidation is provided within the protein microenvironment.

# Enhanced Photostability of the Anthracene Chromophore in Aqueous Medium upon Protein Encapsulation\_2010

By use of electrostatic interactions of dye molecules and poly(diallyldimethylammonium chloride) (PDDA), the spin-coating technique has been successfully applied to the preparation of stable J-aggregate thin films of thiacarbocyanine dyes on a polycarbonate or quartz plate. The J-aggregate thin films were prepared by the spin-coating of PDDA aqueous solution on dye thin films prepared on a substrate by the spin-coating of 2,2,3,3-tetrafluoro-1-propanol solution of dyes. Photophysical properties of the dye thin films and J-aggregate thin films were studied by measuring the fluorescence spectra, quantum yields, and lifetimes. Coherent size of the J-aggregates was estimated to be 3−12 by means of the absorption bandwidth (full width at half maximum) or radiative lifetime. Photostability of the J-aggregate thin films was also studied in terms of photodegradation efficiency under argon and oxygen in comparison with the dye thin films, and J-aggregate thin films were found to be more stable than the corresponding dye thin films.

# Photophysical Property and Photostability of J-Aggregate Thin Films of Thiacyanine Dyes Prepared by the Spin-Coating Method\_2008

The tyrosine corner is proposed as a featured element to enhance photostability in human γB-crystallin when exposed to UV irradiation. Different ultrafast processes were studied by multiconfigurational quantum chemistry coupled to molecular mechanics: photoinduced singlet–singlet energy, electron and proton transfer, as well as population and evolution of triplet states. The minimum energy paths indicate two possible UV photoinduced events: forward–backward proton-coupled electron transfer providing to the system a mechanism for ultrafast internal conversion, and energy transfer, leading to fluorescence or phosphorescence. The obtained results are in agreement with the available experimental data, being in line with the proposed photoinduced processes for the different tyrosine environments within γB-crystallin.

# Photostability Mechanisms in Human γB-Crystallin: Role of the Tyrosine Corner Unveiled by Quantum Mechanics and Hybrid Quantum Mechanics/Molecular Mechanics Methodologies\_2012

Several fluoroquinolone antibacterial agents exhibit an adverse phototoxic effect in humans and are photo-cocarcinogenic in mice. The UV-induced production of reactive oxygen species plays a role in the toxicity and may be involved in carcinogenicity. Four fluoroquinolones were examined for the ability to photochemically produce oxidative damage in naked DNA. The major structural difference in the fluoroquinolones that would have an effect on their photostability is the functionality at the 8-position. At this position, 1-cyclopropyl-7-(2,8-diazbicyclo[4.3.0]non-8-yl)-6,8-difluoro-1,4-dihydro-4-oxo-3-quinolinecarboxylic acid (BAY y3118) contains a chlorine atom, lomefloxacin a fluorine atom, ciprofloxacin a proton, and moxifloxacin a methoxy group. The formation of 8-oxo-7,8-dihydro-2‘-deoxyguanosine (8-oxodGuo) in calf thymus DNA was assessed by HPLC with electrochemical detection, and strand breaks were measured in pBR322 with agarose gel electrophoresis. The relative photolability of the fluoroquinolones correlated to the extent of production of 8-oxodGuo and strand breaks, with both UVA and UVB irradiation, in the following order:  BAY y3118 ∼ lomefloxacin > ciprofloxacin > moxifloxacin. Experiments were performed to determine whether the mechanism of damage was due to a type I (radical) or type II (singlet oxygen) pathway. Nitrogen depletion of oxygen resulted in a decrease in the extent of formation of 8-oxodGuo, suggesting that oxygen was involved. The use of selective radical or singlet oxygen inhibitors was inconclusive with respect to which pathway was involved. The use of D2O as a solvent, which would extend the lifetime of singlet oxygen, suggested that this species is involved in the formation of 8-oxodGuo by moxifloxacin and ciprofloxacin, but not by lomefloxacin and BAY y3118. Similarly, it was found that singlet oxygen was not involved in strand break formation. Thus, the evidence suggests that fluoroquinolones can photochemically produce DNA damage by both type I and type II mechanisms.

# Different Mechanisms for the Photoinduced Production of Oxidative DNA Damage by Fluoroquinolones Differing in Photostability\_1999

Layered double hydroxide-quantum dot (LDH-QD) composites are synthesized via a room temperature LDH formation reaction in the presence of QDs. InP/ZnS (core/shell) QD, a heavy metal free QD, is used as a model constituent. Interactions between QDs (with negative zeta potentials), decorated with dihydrolipoic acids, and inherently positively charged metal hydroxide layers of LDH during the LDH formations are induced to form the LDH-QD composites. The formation of the LDH-QD composites affords significantly enhanced photoluminescence quantum yields and thermal- and photostabilities compared to their QD counterparts. In addition, the fluorescence from the solid LDH-QD composite preserved the initial optical properties of the QD colloid solution without noticeable deteriorations such as red-shift or deep trap emission. Based on their advantageous optical properties, we also demonstrate the pseudo white light emitting diode, down-converted by the LDH-QD composites.

# Strategy for Synthesizing Quantum Dot-Layered Double Hydroxide Nanocomposites and Their Enhanced Photoluminescence and Photostability\_2012

We have successfully utilized epoxyisophorone ring-opening chemistry to efficiently incorporate the butylthio group to the phenyltetraene bridge of highly efficient nonlinear optical chromophores in high overall yield. By following the guidance of Dewar’s rules, the sulfur atom functions as a moderate π-accepting group at a starred position of the conjugated bridge. Several of very critical material parameters of the phenyltetraenic chromophores for device applications have been intrinsically and simultaneously improved through such a simple and straightforward engineering of molecular structures. Compared with the nonsubstituted analogue 2, thiolated chromophore 1 achieves higher molecular hyperpolarizability (34%), enhanced E-O coefficient (38%), significantly improved photochemical stability against 1O2 (by an order of magnitude), and better optical transparency (17 nm blue-shifted λmax absorption spectrum).

# Donor−Acceptor Thiolated Polyenic Chromophores Exhibiting Large Optical Nonlinearity and Excellent Photostability\_2008

For a molecule to survive evolution and to become a key building block in nature, photochemical stability is essential. The photolytically weak S–S bond does not immediately seem to possess that ability. We mapped the real-time motion of the two sulfur radicals that result from disulfide photolysis on the femtosecond time scale and found the reason for the existence of the S–S bridge as a natural building block in folded structures. The sulfur atoms will indeed move apart on the excited state but only to oscillate around the S–S center of mass. At long S–S distances, there is a strong coupling to the ground state, and the oscillatory motion enables the molecules to continuously revisit that particular region of the potential energy surface. When a structural feature such as a ring prevents the sulfur radicals from flying apart and thus assures a sufficient residence time in the active region of the potential energy surface, the electronic energy is converted into less harmful vibrational energy, thereby restoring the S–S bond in the ground state.

# Surprising Intrinsic Photostability of the Disulfide Bridge Common in Proteins\_2012

In this work, highly sensitive discrimination of nerve agent and sulfur mustard simulants is achieved by using photostable and fluorescent coassembled nanofibers from molecules 1 and 2. We demonstrate that the introduction of 2 as a Förster resonance energy transfer (FRET) acceptor not only enhances the photostability and emission efficiency compared to individual 1 nanofibers but also induces different binding interactions between analytes and 1–2 coassembled nanofibers and thereby distinct fluorescence quenching behaviors used for the discrimination of nerve agent and sulfur mustard simulants. Our findings represent an important advance toward sensitive detection and discrimination of chemical warfare agents (CWAs).

# Sensitive Discrimination of Nerve Agent and Sulfur Mustard Simulants Using Fluorescent Coassembled Nanofibers with Förster Resonance Energy Transfer-Enhanced Photostability and Emission\_2019

A theoretical CASSCF study of the reaction path for excited-state intramolecular proton transfer (ESIPT) for a model system derived from the UV absorber 2-(2‘-hydroxyphenyl) benzotriazole without the fused benzo ring on the triazole has been carried out. A planar reaction path can be optimized but is shown to have no physical significance. The true reaction path involves twisted geometries. Adiabatic proton transfer is triggered by a charge-transfer from the phenol to the triazole group, and is followed by radiationless decay at the keto form. Along the nonplanar reaction path, there is a coupled proton and electron transfer in a manner similar to tryptophan. This rationalizes unexpected experimental results on the effect of electron withdrawing substituent groups on the photostability. The coupled proton and electron transfer is followed by a barrierless relaxation in the ground state to recover the enol form. An alternative photostabilization pathway from a phenyl localized state has also been documented and is similar to the channel 3 decay pathway in benzene photochemistry. Additionally, a long-lived intermediate for a twisted intramolecular charge-transfer (TICT) state has been identified as the species potentially responsible for the increase of blue fluorescence in strongly polar media.

# Theoretical Study of Benzotriazole UV Photostability:  Ultrafast Deactivation through Coupled Proton and Electron Transfer Triggered by a Charge-Transfer State\_2004

The relatively unexplored luminophore architecture [Ir(N^N^N)(C^N)L]+ (N^N^N = tridentate polypyridyl ligand, C^N = 2-phenylpyridine derivative, and L = monodentate anionic ligand) offers the stability of tridentate polypyridyl coordination along with the tunability of three independently variable ligands. Here, a new family of these luminophores has been prepared based on the previously reported compound [Ir(tpy)(ppy)Cl]+ (tpy = 2,2′:6′,2″-terpyridine and ppy = 2-phenylpyridine). Complexes are obtained as single stereoisomers, and ligand geometry is unambiguously assigned via X-ray crystallography. Electrochemical analysis of the materials reveals facile HOMO modulation through ppy functionalization and alteration of the monodentate ligand’s field strength. Emission reflects similar modulation shifting from orange to greenish-blue upon replacement of chloride with cyanide. Many of the new compounds exhibit impressive room temperature phosphorescence with lifetimes near 3 μs and quantum yields reaching 28.6%. Application of the new luminophores as photosensitizers for photocatalytic hydrogen generation reveals that their photostability in coordinating solvent is enhanced as compared to popular [Ir(ppy)2(bpy)]+ (bpy = 2,2′-bipyridine) photosensitizers. Yet, the binding of their monodentate ligand emerges as a source of instability during the redox processes of cyclic voltammetry and mass spectrometry. DFT modeling of electronic structure is provided for all compounds to elucidate experimental properties.

# [Ir(N^N^N)(C^N)L]+: A New Family of Luminophores Combining Tunability and Enhanced Photostability\_2014

The development of near-infrared (NIR) dyes with desirable photophysical characteristics for tumor therapy is highly expected at present. In this report, IR-780 iodide was loaded by the mercaptopropionic acid grafted poly(ethylene glycol)-block-poly(ε-caprolactone)-block-poly(allyl glycidyl ether) [mPEG5K-PCL10K-PAGE6 (MPA)] copolymer to form nanomicelles (IR-780@TBMPA) in aqueous solution. On account of the hydrophobic and electrostatic interaction between mPEG5K-PCL10K-PAGE6 (MPA) and IR-780, the IR-780@TBMPA micelle was structurally stable with improved solubility, light stability and biocompatibility. The encapsulation of IR-780 indicated no influence on its original physicochemical property, showing good optical and thermal characteristics. The drug-loaded micelles had appropriate microscopic size for endocytosis, displaying significant cytotoxicity to HeLa cells under NIR laser irradiation. In addition, the phototoxicity generated by photothermal and photodynamic effect of IR-780@TBMPA under 808 nm laser irradiation was also investigated by reactive oxygen species (ROS) detection and flow cytometry. Furthermore, the superior accumulation of IR-780@TBMPA in tumor tissues provided sufficient hyperthermia to kill tumor cells, indicating its potential in cancer clinical therapy.

# Photostability Highly Improved Nanoparticles Based on IR-780 and Negative Charged Copolymer for Enhanced Photothermal Therapy\_2018

Ultrafast time-resolved fluorescence spectroscopy has been used to investigate the excited-state dynamics of the basic eumelanin building block 5,6-dihydroxyindole-2-carboxylic acid (DHICA), its acetylated, methylated, and carboxylic ester derivatives, and two oligomers, a dimer and a trimer in the O-acetylated forms. The results show that (1) excited-state decays are faster for the trimer relative to the monomer; (2) for parent DHICA, excited-state lifetimes are much shorter in aqueous acidic medium (380 ps) as compared to organic solvent (acetonitrile, 2.6 ns); and (3) variation of fluorescence spectra and excited-state dynamics can be understood as a result of excited-state intramolecular proton transfer (ESIPT). The dependence on the DHICA oligomer size of the excited-state deactivation and its ESIPT mechanism provides important insight into the photostability and the photoprotective function of eumelanin. Mechanistic analogies with the corresponding processes in DNA and other biomolecules are recognized.

# Role of Solvent, pH, and Molecular Size in Excited-State Deactivation of Key Eumelanin Building Blocks: Implications for Melanin Pigment Photostability\_2008

We herein report a kind of one-dimensional biocompatible fluorescent silicon nanorods (SiNRs) with tunable lengths ranging ∼100–250 nm, which can be facilely prepared through one-pot microwave synthesis. In addition to the strong fluorescence (quantum yield value: ∼15%) and negligible toxicity, the resultant SiNRs exhibit excitation wavelength-dependent photoluminescence whose maximum emission wavelength ranges from ∼450 to ∼600 nm under serial excitation wavelengths from 390 to 560 nm, providing feasibility for multicolor biological imaging. More significantly, the SiNRs are ultrahighly photostable, preserving strong and nearly unchanged fluorescence under 400 min high-power UV irradiation, which is in sharp contrast to severe fluorescence quenching of organic dyes (e.g., FITC) or II–VI quantum dots (QDs) (e.g., CdTe QDs and CdSe/ZnS QDs) within 15 or 160 min UV treatment under the same experiment conditions, respectively. Taking advantage of these attractive merits, we further exploit the SiNRs as a novel type of color converters for the construction of white light-emitting diodes (LED), which is the first proof-of-concept demonstration of LED device fabricated using the one-dimensional fluorescent silicon nanostructures.

# One-Dimensional Fluorescent Silicon Nanorods Featuring Ultrahigh Photostability, Favorable Biocompatibility, and Excitation Wavelength-Dependent Emission Spectra\_2016

Previous work has shown that pentacoordinated bromine compounds have their lowest excited electronic states shifted to the blue relative to monocoordinated bromine molecules, and that this shift may be large enough to render them photostable in the lower stratosphere. Our earlier work has also shown that certain pentacoordinated bromine compounds are thermodynamically stable relative to their mono- or tricoordinated isomers, suggesting that if a bromine stratospheric reservoir species exists, it may be a pentacoordinated compound. In this study we have examined the singlet and triplet excited electronic states of several bromine compounds, using time dependent density functional theory, to assess their photostability under stratospheric conditions and in order to elucidate the nature of lowest excited states in mono-, tri-, and pentacoordinated bromine molecules. The triplet states have been included due to the strong spin−orbit mixing in bromine. We have found several pentacoordinated bromine/oxygen compounds that could be photostable in the lower stratosphere, but we have also found that monovalent bromine compounds where the bromine atom is bonded to an atom with no lone-pair p-electrons is far and away the most photostable. Attachment/detachment electron density plots have been useful in ascertaining the nature of the excited electronic states and their likely path to photodissociation.

# Search for Stratospheric Bromine Reservoir Species:  Theoretical Study of the Photostability of Mono-, Tri-, and Pentacoordinated Bromine Compounds\_2005

Photobleaching and biotoxicity are the main bottlenecks for organic fluorescent dyes applied in real-time dynamic monitoring of living cells. Here, an unnatural amino acid, 4-nitro-3-phenyl-l-alanine (NPA), was used as a scaffold to covalently link a near-infrared fluorophore Cy5.5 and an amphiphilic polypeptide, poly[oligo(ethylene glycol) methyl ether methacrylate]-block-poly[2-amino-N4-(2-diisopropylamino-ethyl)-l-aspartic acid] (P(OEGMA)21-P(Asp)16-iPr), was then conjugated for increasing the photostability and improving the biocompatibility simultaneously. The protective agent of NPA can service as an effective triplet state quenching by intramolecular electron transfer between Cy5.5 and NPA. The less sensitivity of the electron-transfer process for molecular oxygen makes it an ideal photostabilized strategy for fluorophores applied in live-cell imaging. Bonding to copolymer is a common way for hydrophobic dyes to expand their application in biomedical imaging and increase their functionality, depending on the delivery system. The results indicate that Cy5.5–NPA-linked polypeptide copolymer exhibited an enhanced photostability and an excellent biocompatibility, which means this scaffolding strategy has a potential application in fluorescence-guided surgery, lived-cell imaging, and super-resolution microscopy.

# Self-Healing Organic Fluorophore of Cyanine-Conjugated Amphiphilic Polypeptide for Near-Infrared Photostable Bioimaging\_2018

# Emission characteristics and photostability of N,N'-bis(2,5-di-tertbutylphenyl)-3,4:9,10-perylenebis(dicarboximide)\_1988

The objective of this work was to increase color yield of direct dyes on cotton with the aid of grafted quaternary ammonium monomers. Plasma-induced graft polymerization of diallyldimethylammonium chloride (DADMAC) and [2-(acryloyloxy)ethyl]trimethylammonium chloride (AOETMAC) on cotton followed by dyeing with direct dyes was studied using different concentrations of the monomers and plasma conditions, and the color yield was evaluated using K/S measurements. Colorfastness and staining after laundering were evaluated using the standard grayscale. A significant increase of 149% in color yield was achieved when 30 g/L of DADMAC was used. 100–300% increase in K/S was achieved when ∼20 g/L of AOETMAC was used. To enhance the wash and lightfastness of the direct dyes on cotton, plasma-induced graft polymerization of 1,1,2,2-tetrahydroperfluorododecyl acrylate was achieved on the dyed cotton and showed considerable enhancement in both the wash and lightfastness.

# Plasma Induced Graft Polymerization of Cationic and Fluorocarbon Monomers into Cotton: Enhanced Dyeability and Photostability\_2016

Novel CdS/ZnFe2O4 composites were prepared through a two-step hydrothermal process. The homogeneous ZnFe2O4 nanoparticles are decorated on the self-assembled CdS spheres. Compared to those of pure CdS and blank ZnFe2O4, the photocatalytic activity and stability of the magnetically separable CdS/ZnFe2O4 composites are considerably increased. The results of photoluminescence and electrochemical impedance spectroscopy further validate that the performance enhancement results from the construction of heterojunction structure, leading to high charge separation efficiency. On the basis of the calculation and the trapping test, a heterojunction photocatalytic mechanism is proposed.

# Magnetically Separable CdS/ZnFe2O4 Composites with Highly Efficient Photocatalytic Activity and Photostability under Visible Light\_2018

In this work we build on prior studies of the novel water-soluble cationic conjugated polymer known as “P2” (poly{2,5-bis[3-(N,N,N-triethylammonium bromide)-1-oxapropyl]-1,4-phenylenevinylene}) with a focus on its incorporation into thin films for such applications as photovoltaics or electroluminescent devices. Multilayer assemblies were constructed using P2, the anionic surfactant sodium dodecyl sulfate (SDS), and the polyanion poly(sodium 4-styrene-sulfonate) (PSS) using the technique of layer-by-layer electrostatic self-assembly (LBL-ESA). SDS was observed to affect the layer thicknesses and absorbance characteristics of the films. We show that the optical properties and photo-oxidative resistance can be improved by varying the SDS content in the assemblies. Specifically, the surfactant-complexed poly(p-phenylenevinylene) (PPV) shows an enhanced absorption at longer wavelengths as well as improved photostability. Therefore, our work may have broad implications on the development of stable PPV-based materials in general and their efficient integration into thin films technologies.

# Controlling Layer Thickness and Photostability of Water-Soluble Cationic Poly(p-phenylenevinylene) in Multilayer Thin Films by Surfactant Complexation\_2008

# Toward the photostability mechanism of intramolecular hydrogen bond systems. The photophysics of 1'-hydroxy-2'-acetonaphthone\_1993

Currently, the stability issue of the perovskite solar cells (PSCs) is one of the most critical obstacles in the commercialization of PSCs. Although incredible advances in the photovoltaic efficiencies of PSCs have been achieved in the past few years, research on the stability of PSCs has been relatively less explored. In this study, a new kind of CdS hole-blocking layer replacing the traditional compact TiO2 layer is developed to improve the photostability of PSCs because the intrinsic oxygen vacancies of the TiO2 surface are suspected to be the main cause for the photoinduced degradation of PSCs. As a result, PSCs with the CdS layer exhibit considerably improved photostability, maintaining over 90% of the initial efficiency after continuous sunlight illumination for 12 h, while the TiO2 PSC retains only 18% of the initial efficiency under the same conditions. Charge-transfer characteristics related to photodegradation are investigated by various analyses including electrochemical impedance spectroscopy and open-circuit voltage decay and time-resolved photoluminescence decay measurements. the CdS PSC exhibits negligible degradation in the charge-carrier dynamics, while the TiO2 PSC suffers from severely damaged characteristics like increased charge recombination rate, charge-transfer resistance, and reduced charge extraction rate.

# Novel CdS Hole-Blocking Layer for Photostable Perovskite Solar Cells\_2016

Replacement of the pyrethronyl alcohol portion of the natural pyrethrins with the 5-benzyl-3-furylmethyl moiety gave bioresmethrin, a synthetic pyrethroid of high potency and safety but with limited photostability. Introduction of novel substituents at the 3-position of the cyclopropane ring then led to the discovery of insecticidally active compounds with greatly improved potency. Systematic changes of both the alcohol and acid components gave second-generation pyrethroids (permethrin, cypermethrin, and deltamethrin) with improved potency and photostability suitable for agricultural use. Metabolic studies showed that the photostabilized compounds remained biodegradable. Deltamethrin, discovered in 1974, was the cream of the crop and remains 36 years later as one of the most important synthetic pyrethroid insecticides.

# Deltamethrin: The Cream of the Crop\_2010

Two highly luminescent and water-soluble Eu(III) complexes, Eu1 and Eu2, based on novel carboxyl-functionalized 1,5-naphthyridine derivatives 8-hydroxy-1,5-naphthyridine-2-carboxylic acid (H2L1) and 7-cyano-8-hydroxy-1,5-naphthyridine-2-carboxylic acid (H2L2), respectively, are designed and synthesized. The crystal structure of Eu2 indicates that the central Eu(III) ion is nine-coordinated by three tridentate ligands (O^N^O). Both Eu1 and Eu2 show strong luminescence in aqueous solution with quantum yields (lifetimes) of 28% (1.1 ms) and 14% (0.76 ms), respectively. The chelates display unique UV-light stability in solution and remain highly emissive after 100 min of strong UV irradiation (∼300 W·m–2 at 345 nm). Moreover, they exhibit reversible luminescence intensity changes with varied pH values, and the response mechanism is investigated. “Turn-on” of the Eu(III) emission upon increasing pH is realized by ligand structure change from keto to enol anion form, resulting in red-shifted absorption band and suppressed quenching from solvents and N–H vibration upon deprotonating. The results show that these novel Eu(III) complexes are quite intriguing for potential application as bioimaging agents and pH probes.

# Water-Soluble and Highly Luminescent Europium(III) Complexes with Favorable Photostability and Sensitive pH Response Behavior\_2016

To accurately monitor the variations of lysosomal nitric oxide (NO) under physiological condition remains a great challenge for understanding the biological function of NO. Herein, we developed a new chemotype probe, namely, MBTD, for acid-promoted and far-red fluorescence imaging of lysosomal NO in vitro and ex vivo. MBTD was rationally designed by incorporating o-phenylenediamino (OPD) moiety into the donor–acceptor–donor (D-A-D) type fluorophore based on a dual intramolecular charge transfer (ICT) mechanism. Compared to previously reported OPD-based NO probes, MBTD displays several distinct advantages including large stroke shift, huge on–off ratio with minimal autofluorescence, and high NO specificity. Particularly, MBTD exhibits an acid-promoted response to NO with high acid tolerance, which greatly improves the spatial resolution to lysosomal NO by excluding the background noise from other nonacidic organelles. Furthermore, MBTD displayed much longer-lived and more stable fluorescence emission in comparison with the commercialized NO probe. MBTD was employed for ratiometric examination of the exogenous or endogenous NO of macrophages. More importantly, MBTD was able to detect the variation of lysosomal NO level in an acute liver injury mouse model ex vivo, implying the potential of MBTD for real-time monitoring the therapeutic efficacy of drug candidates for the treatment of acute liver injury. MBTD as a novel type of NO probe might open a new avenue for precisely sensing lysosomal NO-related pathological and therapeutic process.

# Acid-Promoted D-A-D Type Far-Red Fluorescent Probe with High Photostability for Lysosomal Nitric Oxide Imaging\_2018

The doping strategy of hybrid perovskites is being extensively explored not only for higher efficiency but also to overcome issues in photovoltaic materials such as self-degradation pathways in an ambient atmosphere or under visible irradiation. Here, BiI3 is introduced in the synthesis of MAPbI3 films (MA: CH3–NH3+) to stabilize the material. Around 25% of nominal Bi3+ is accommodated in the perovskite structure, producing a shrinking of the unit cell and a small increase of the band gap. The presence of empty Bi gap states quenches the 770 nm red interband emission and results in a near-infrared emission at 1100 nm. However, high enough visible irradiation density induces a progressive segregation of Bi3+ out of the perovskite lattice and promotes the re-emergence of the red emission. This emission is blue-shifted, and its intensity increases strongly with time until it reaches a saturation value which remains stable in the transformed films for extremely high power densities, around 1000 times higher than for undoped samples. We propose that the underlying processes include the formation of BiI3 and BiOI, probably at the surface of the crystals, hampering the usual decomposition pathways into PbI2 and PbOx for undoped MAPbI3. These results provide a new path for obtaining highly stable materials which would allow an additional boost of hybrid perovskite-based optoelectronics.

# Huge Photostability Enhancement in Bismuth-Doped Methylammonium Lead Iodide Hybrid Perovskites by Light-Induced Transformation\_2019

The application of pesticide microcapsules (MCs) in agriculture is becoming more and more popular. In this study, the effects of different wall materials on the stomach toxicity, contact toxicity, length of efficacy, and photolysis characteristics of pesticide microcapsules were investigated. The results showed that microencapsulation reduced the stomach and contact toxicities of phoxim and prolonged the efficacy of this light-sensitive chemical in the greenhouse test. Neither of the degradation curves for microencapsulated phoxim under ultraviolet light fit a first-order model, although the emulsifiable concentrate (EC) degradation curve fit it well. The phoxim-loaded polyurea microcapsules (PUA-MCs) showed significantly increased UV-resistance ability, stomach toxicity, and contact toxicity compared with the phoxim-loaded urea–formaldehyde microcapsules (UF-MCs). These experiments indicated that it is crucial to select the appropriate wall materials for pesticide microcapsules on the basis of application sites and physicochemical properties of pesticide active ingredients.

# Phoxim Microcapsules Prepared with Polyurea and Urea–Formaldehyde Resins Differ in Photostability and Insecticidal Activity\_2016

The dual-emissive properties of solid-state difluoroboron β-diketonate-poly(lactic acid) (BF2bdkPLA) materials have been utilized for biological oxygen sensing. In this work, BF2dbm(X)PLA materials were synthesized, where X = H, F, Cl, Br, and I. The effects of changing the halide substituent and PLA polymer chain length on the optical properties in dilute CH2Cl2 solutions and solid-state polymer films were studied. These luminescent materials show fluorescence, phosphorescence, and lifetime tunability on the basis of molecular weight, as well as lifetime modulation via the halide substituent. Short BF2dbm(Br)PLA (6.0 kDa) and both short and long BF2dbm(I)PLA polymers (6.0 or 20.3 kDa) have fluorescence and intense phosphorescence ideal for ratiometric oxygen sensing. The lighter halide-dye polymers with hydrogen, fluorine, and chlorine substitution have longer phosphorescence lifetimes and can be utilized as ultrasensitive oxygen sensors. Photostability was also analyzed for the polymer films.

# Tailoring Oxygen Sensitivity with Halide Substitution in Difluoroboron Dibenzoylmethane Polylactide Materials\_2015

Photostability of organic photovoltaic devices represents a key requirement for the commercialization of this technology. In this field, ZnO is one of the most attractive materials employed as an electron transport layer, and the investigation of its photostability is of particular interest. Indeed, oxygen is known to chemisorb on ZnO and can be released upon UV illumination. Therefore, a deep analysis of the UV/oxygen effects on working devices is relevant for the industrial production where the coating processes take place in air and oxygen/ZnO contact cannot be avoided. Here we investigate the light-soaking stability of inverted organic solar cells in which four different solution-processed ZnO-based nanoparticles were used as electron transport layers: (i) pristine ZnO, (ii) 0.03 at %, (iii) 0.37 at %, and (iv) 0.8 at % aluminum-doped AZO nanoparticles. The degradation of solar cells under prolonged illumination (40 h under 1 sun), in which the ZnO/AZO layers were processed in air or inert atmosphere, is studied. We demonstrate that the presence of oxygen during the ZnO/AZO processing is crucial for the photostability of the resulting solar cell. While devices based on undoped ZnO were particularly affected by degradation, we found that using AZO nanoparticles the losses in performance, due to the presence of oxygen, were partially or totally prevented depending on the Al doping level.

# Enhanced Ultraviolet Stability of Air-Processed Polymer Solar Cells by Al Doping of the ZnO Interlayer\_2016

A convenient approach for the direct synthesis of meso-substituted thiazole orange (meso-TO) analogues has been unprecedentedly developed through the AlCl3-catalyzed reaction of parent TO with benzyl alcohol derivatives. Single-crystal X-ray structures show that the prepared new meso-TO analogues are nonplanar, forming a sharp contrast to planar TO. The spectral properties show that nonplanar meso-TO analogues do not aggregate, existing in monomer form (M) in PBS buffer, and have little effect of solvatochromism in different solvents. In comparison with the parents, meso-TO analogues exhibit a large Stokes shift, excellent light fastness, and inertness to singlet oxygen. A cellular association study demonstrates that incorporation of a benzyl group at the meso position methine of parent TO can decrease the cytotoxicity, change staining area in cells, and emit long-wavelength fluorescence for an extended time, which are useful for the development of smarter TOs for imaging in biological science.

# Nonplanar Monocyanines: Meso-Substituted Thiazole Orange with High Photostability and Their Synthetic Strategy as well as a Cell Association Study\_2016

We report the investigation of the air photostability of benzo[1,2-b:4,5-b′]dithiophene (BDT) based conjugated polymers using UV–visible spectroscopy, X-ray photoelectron spectroscopy, gel permeation chromatography, and nuclear magnetic resonance spectroscopy. Three low band gap alternating D–A copolymers consisting of 3-fluoro-2-heptylcarbonylthieno[3,4-b]thiophene and alkyl-substituted BDT, alkoxy-substituted BDT, or dithienosilole, respectively, were prepared for investigating their photovoltaic performance and photostability. After only two hours of simultaneous exposure to light and air, the main absorption peak of the polymer films containing BDT units blue-shifted and its intensity dramatically decreased. We demonstrated that the BDT unit underwent dramatic structural change under illumination in air by reacting with the oxygen molecules at the excited state, leading to the disruption of the main-chain conjugation of the polymer. As a result, the color of the alkyl-BDT based polymer film permanently changed from deep blue to light yellow. In contrast, the dithienosilole based polymer was quite stable when treated under the same condition with negligible change in the absorption spectrum.

# Degradation Mechanism of Benzodithiophene-Based Conjugated Polymers when Exposed to Light in Air\_2012

Melanin is a ubiquitous natural pigment that protects living organisms from intense sunlight. Although synthetic melanin with different sizes and morphologies has been developed for UV-shielding polymers, studies can rarely be found regarding their natural counterparts. In this study, the natural melanin (NM) granules were isolated from conventional textile scraps such as yak and alpaca hair wastes and well characterized. This was followed by integrating them with TiO2 nanoparticles through hydrogen bonding using a simple physical mixing method, and the resultant NM/TiO2 hybrids were embedded in polyurethane (PU) films. Our results suggested that the PU films containing 2.5 wt % NM/TiO2 hybrids possessed highly efficient UV-shielding ability, improved photostability, and well-maintained transparency. The ultraviolet protection factor (UPF) values of the 2.5 wt %-NM/TiO2/PU composite films were approximately four times higher than those of the 2.5 wt %-TiO2/PU composite films. Moreover, although the 2.5 wt %-NM/TiO2/PU and 1.25 wt %-NM/PU composite films shared a similar UPF value, the transmittance at 550 nm of 2.5 wt %-NM/TiO2/PU was ∼2.5 times higher. Most importantly, the photoinduced chemiluminescence tests proved the excellent photostability of the NM/TiO2/PU composite films. Owing to the abundant natural source of NM, the commercial availability of TiO2, as well as the simple preparation protocol of the NM/TiO2 hybrids, this work highlights the potential of hair-derived NM-based UV-shielding fillers for various polymeric materials.

# Waste-Hair-Derived Natural Melanin/TiO2 Hybrids as Highly Efficient and Stable UV-Shielding Fillers for Polyurethane Films\_2019

Photovoltachromic cells (PVCCs) are of great interest for the self-powered smart windows of architectures and vehicles, which require widely tunable transmittance and automatic color change under photostimuli. Organolead halide perovskite possesses high light absorption coefficient and enables thin and semitransparent photovoltaic device. In this work, we demonstrate co-anode and co-cathode photovoltachromic supercapacitors (PVCSs) by vertically integrating a perovskite solar cell (PSC) with MoO3/Au/MoO3 transparent electrode and electrochromic supercapacitor. The PVCSs provide a seamless integration of energy harvesting/storage device, automatic and wide color tunability, and enhanced photostability of PSCs. Compared with conventional PVCC, the counter electrodes of our PVCSs provide sufficient balancing charge, eliminate the necessity of reverse bias voltage for bleaching the device, and realize reasonable in situ energy storage. The color states of PVCSs not only indicate the amount of energy stored and energy consumed in real time, but also enhance the photostability of photovoltaic component by preventing its long-time photoexposure under fully charged state of PVCSs. This work designs PVCS devices for multifunctional smart window applications commonly made of glass.

# Perovskite Photovoltachromic Supercapacitor with All-Transparent Electrodes\_2016

Melanin is a kind of ubiquitous natural pigment, which serves a variety of protective functions in many organisms. In the present study, natural melanin and synthetic melanin nanoparticles (NPs) were systematically investigated for its potential application in polymeric optical materials. A significant short-wavelength shielding and high visible light transparency polymer nanocomposite was easily obtained via tuning the melanin particle size. In particular, the nanocomposite film with melanin NPs (diameter ≈ 15 nm) loading even as low as 1 wt % blocks most ultraviolet light below 340 nm and still keeps high visible light transparency (83%) in the visible spectrum. More importantly, because of the excellent photoprotection and radical scavenging capabilities of melanin, the resulting polymer nanocomposite exhibits outstanding photostability. In effect, such fantastic melanin NPs is promising for applications in various optical materials.

# Effects of Melanin on Optical Behavior of Polymer: From Natural Pigment to Materials Applications\_2018

Halogenated aromatic compounds (HACs) in the environment have created great concern because of the associated adverse health implications. In this study we investigated the atmospheric behavior and exposure risk of brominated polycyclic aromatic hydrocarbons (BrPAHs) larger than three rings which were associated with particles in the urban air in Japan, and which were discovered as novel HACs in the air. Furthermore, the ambient levels of chlorinated polycyclic aromatic hydrocarbons (ClPAHs) and PAHs, in addition to BrPAHs, were also simultaneously investigated to emphasize the differences. Seven of 11 target BrPAHs were newly detected from the urban air samples in Japan between 2004 and 2005. Of the BrPAHs detected, 5,7-Br2BaA was most abundant (mean concentration, 8.7 pg m−3), followed by 7,12-Br2BaA (6.3 pg m−3) and 6-BrBaP (3.3 pg m−3). The mean concentrations of total BrPAHs, ClPAHs, and PAHs detected were 8.6 pg m−3, 15.2 pg m−3, and 1.2 ng m−3, respectively, which showed that concentrations of such halogenated PAHs (Br-/Cl-PAHs) tended to be approximately 100-fold lower than PAHs. The BrPAHs had photolysis rates that were relatively faster than the corresponding ClPAHs. Comparing the ambient profiles among the PAH congeners suggested that ambient BrPAHs that came from the specific local emission sources differed from ClPAHs and PAHs, and/or could be driven by various seasonal factors, including photodecay processes. Most of the BrPAHs used showed inherent AhR-mediated activities. Toxic equivalents based on the relative potencies of each AhR activity and the ambient concentrations showed that either BrPAHs or ClPAHs accounted for a smaller proportion (∼1%) of the total.

# Discovery of Novel Halogenated Polycyclic Aromatic Hydrocarbons in Urban Particulate Matters: Occurrence, Photostability, and AhR Activity\_2009

Patterned silver nanocap arrays (PSNAs) prepared on porous anodic alumina templates by a simple coating technique yield enhanced sensitivity and stability in cellular fluorescence imaging. Microstructural analysis, surface-enhanced Raman scattering mapping, and finite difference time domain simulation indicate that the hot spots are evenly distributed on the substrate. Ag1522 or Chinese Hamster Ovary cells are labeled by phalloidin-fluorscein isothiocyanate (P-FITC) on the cytoskeletons and the fluorescence signals from the fluorophores bound on the cell cytoskeletons on the PSNAs are enhanced 8-fold compared to those on glass used in conventional imaging. In addition to the intensity enhancement, the photostability is improved dramatically. Spectral analysis suggests that the PSNAs can create more excitons in the light-emitting P-FITC because of plasmon resonance energy transfer from the silver nanocaps to the nearby P-FITC. They can also act as plasmonic antennae by converting a part of the nonradiative near-field emission from the fluorophores to the far field consequently enhancing the emission.

# High-Sensitivity and Stable Cellular Fluorescence Imaging by Patterned Silver Nanocap Arrays\_2010

Linear steady-state and time-resolved spectroscopic properties, degenerate two-photon absorption (2PA) spectra, and photochemical stability of IrIII complexes TCQ[IrIII(ppz)2]n, (TCQ = tricycloquinazoline; ppz = 1-phenylpyrazole; n = 1 (1), n = 2 (2), and n = 3 (3)) are presented for liquid solutions. The analysis of the linear photophysical properties revealed the nature of the observed dual-component fluorescence–phosphorescence emission of 1–3 at room temperature. The values of 2PA cross sections were determined by open aperture Z-scans using a 1 kHz femtosecond laser system. The specific dependence of the 2PA efficiency on the number of ppz ligand units in 1–3 was determined. The quantum yields, Φph, for photochemical decomposition of TCQ[IrIII(ppz)2]n complexes were obtained for the first time using the absorption method [Corredor, C. C.; J. Photoch. Photobio. A 2006, 184, 105−112] with continuous wave laser irradiation, and the highest stability of Φph ≈ 4 × 10–6 was shown for 2 in toluene.

# Dual Emissive Multinuclear Iridium(III) Complexes in Solutions: Linear Photophysical Properties, Two-Photon Absorption Spectra, and Photostability\_2018

The phototautomerization mechanism of a model nitro enamine (NEA) chromophore (incorporated in the structure of a highly photolabile pesticide, tetrahydro-2-(nitromethylene)-2H-1,3-thiazine) has been studied using complete active space self-consistent field reaction path computations. The optically accessible 1ππ\* excited state of NEA involves separation of charge and correlates diabatically with the ground state of the tautomerized acinitro imine (ANI) form. For optimum photostabilization, the 1ππ\* state of NEA should be S1:  in this case, the tautomer would be efficiently formed via a diabatic intramolecular proton-transfer pathway passing through an S1/S0 conical intersection, followed by a facile thermal back proton-transfer reaction. However, in NEA itself the lowest excited states correspond to nitro group 1nπ\* states, and there are additional surface crossings that provide a mechanism for populating the 1nπ\* manifold. The above results indicate that the high photolability observed for the pesticide [Kleier, D.; Holden, I.; Casida, J. E.; Ruzo, L. O. J. Agric. Food Chem. 1985, 33, 998−1000] has to be ascribed to photochemistry originating on the 1nπ\* manifold of states, populated indirectly from the 1ππ\* state.

# Photostability versus Photodegradation in the Excited-State Intramolecular Proton Transfer of Nitro Enamines:  Competing Reaction Paths and Conical Intersections\_2007

# 3-(3,3-Dihalo-2-propenyl) analogs of allethrin and related pyrethroids: synthesis, biological activity, and photostability\_1983

# Correction. Toward the Photostability Mechanism of Intramolecular Hydrogen Bond Systems. The Photophysics of 1'-Hydroxy-2'-acetonaphthone\_1993

Lanthanide-based photoluminescent emitters have gained strong attention over the past years because they provide certain advantages over organic fluorophores. Especially their excellent photostability has given rise to efforts in applying lanthanides for stimulated emission depletion (STED) nanoscopy. While STED has been demonstrated for dual lanthanide-based upconversion nanoparticles and single lanthanide ions embedded in yttrium aluminum garnet, a proof of the general lanthanide applicability for STED nanoscopy is still missing. Here we show that doping sodium yttrium fluoride (NaYF4) nanocrystals with either dysprosium or europium ions leads to working Stokes-side STED labels. The vast number of states inherent to most of the lanthanide ions should also allow the discovery of other lanthanides as potential Stokes-side STED labels in similar or alternative hosts.

# Lanthanide-Doped Nanoparticles for Stimulated Emission Depletion Nanoscopy\_2019

The photostability, photodestructive efficacy, two-photon excitation cross section, and two-photon fluorescence of gold nanoparticles conjugated with a hydrophilic photosensitizer, indocyanine green, via multiphoton laser exhibited an increased size effect in methicillin-resistant Staphylococcus aureus and A549 cancer cells that was dependent on the size of multifunctional gold nanomaterials, but the effect only occurred when nanomaterials within 100 nm in diameter were used. Besides, the enhanced effectiveness of photodestruction, photostability, and contrast probe indicated an additive effect in the therapeutic and imaging efficiency of multifunctional gold nanomaterials. Consequently, the preparation of the multifunctional gold nanomaterials and their use in biomedical applications via multiphoton laser is an alternative and potential therapeutic approach for killing bacteria and for ablating cancer cells.

# Effect of Size-Dependent Photodestructive Efficacy by Gold Nanomaterials with Multiphoton Laser\_2015

# The nature of the silica cage as reflected by spectral changes and enhanced photostability of trapped Rhodamine 6G\_1984

Monoclonal antibodies are one of the most useful and ubiquitous affinity reagents used in the biological sciences. Immunostaining of fixed and live cells for microscopy or cytometry measurements frequently employs fluorescently labeled antibodies, in particular fluorescein-labeled antibodies. This dye emits light at a wavelength overlapping with cellular autofluorescence, making it difficult to measure antibody binding to proteins of relatively low copy number or in cells of high green autofluorescence. A number of high affinity fluorescein binding antibodies and antibody domains have been developed that quench the dye’s fluorescence. Using a fluorescein-binding recombinant antibody domain genetically fused to a fluorogen activating protein (FAP), we demonstrate a molecular converter capable of binding and quenching fluorescein, while binding and activating a fluorogenic triarylmethane dye. This reagent converts fluorescein conjugates to far-red fluorescent probes, where cellular autofluorescence is low, improving signal-to-background of cell-based antibody binding measurements by ∼7-fold. Microscopy experiments show colocalization of both fluorescein and MG fluorescence. This dual affinity fluorescein-quenching-FAP can also be used to convert fluorescein to the red fluorescing MG fluorogen on biological molecules other than antibodies.

# A Bifunctional Converter: Fluorescein Quenching scFv/Fluorogen Activating Protein for Photostability and Improved Signal to Noise in Fluorescence Experiments\_2014

Currently, the most efficient perovskite solar cells (PSCs) mainly use planar and mesoporous titanium dioxide (TiO2) as an electron-transport layer (ETL). However, because of its intrinsic photocatalytic properties, TiO2 can decompose perovskite absorber and lead to poor stability under solar illumination (ultraviolet light). Herein, a simplified architectural ETL-free PSC with enhanced efficiency and outstanding photostability is produced by the facile deposition of a bathocuproine (BCP) interlayer. Power conversion efficiency of the ETL-free PSC improves from 15.56 to 19.07% after inserting the BCP layer, which is the highest efficiency reported for PSCs involving an ETL-free architecture, versus 19.03% for the n–i–p full device using TiO2 as an ETL. The BCP interlayer has been demonstrated to have several positive effects on the photovoltaic performances of devices, such as “modulation doping” of the perovskite layer, modification of FTO surface work function, and enhancing the charge-transfer efficiency between FTO and perovskite. Moreover, the BCP-based ETL-free devices exhibit outstanding photostability: the unencapsulated BCP-based ETL-free PSCs retain over 90% of their initial efficiencies after 1000 h of storage in air and maintain 92.2% after 450 h of exposure to full solar irradiation (without a UV filter), compared to only 14.1% in the n–i–p full cells under the same condition.

# Insulated Interlayer for Efficient and Photostable Electron-Transport-Layer-Free Perovskite Solar Cells\_2018

The photocatalytic destruction of methyl orange in aqueous solution has been studied over single crystal ZnO surfaces under UV irradiation. Differences in the apparent reaction rates between the polar surfaces (first order) and the nonpolar ZnO(10−10) surface (zero order) were observed. Reaction rates for different crystallographic orientations showed the highest activity for ZnO(10−10) followed by ZnO(0001)-Zn and the lowest activity for ZnO(000−1)-O surfaces. In addition, the etching of surfaces by photolysis has been studied. For this process, strongly face-dependent behavior was also observed. Possible reasons for the face dependencies are discussed.

# Photocatalytic Degradation of Methyl Orange over Single Crystalline ZnO: Orientation Dependence of Photoactivity and Photostability of ZnO\_2009

Metal nanoclusters consist of a few to a few hundred atoms and exhibit attractive molecular properties such as ultrasmall size, discrete energy levels, and strong fluorescence. Although patterning of these clusters down to the micro- or nanoscale could lead to applications such as high-density data storage, it has been reported only for inorganic matrices. Here we present submicron-scale mask-free patterning of fluorescent silver nanoclusters in an organic matrix. The nanoclusters were produced by direct laser writing in poly(methacrylic acid) thin films and exhibit a broadband emission at visible wavelengths with photostability that is superior to that of Rhodamine 6G dye. This fabrication method could open new opportunities for applications in nanophotonics like imaging, labeling, and metal ion sensing. We foresee that this method can be further applied to prepare other metal nanoclusters embedded in compositionally different polymer matrices.

# Direct Laser Writing of Photostable Fluorescent Silver Nanoclusters in Polymer Films\_2014

Hybrid nanomaterials based on the covalent grafting of silylated naphthopyrans (NPTs) onto silica nanoparticles (SiO2 NPs) were successfully prepared and studied as new photochromic materials. They were prepared by a two-step protocol consisting of (i) NPTs (derivatives from 2H-naphtho[1,2-b]pyran (2H-NPT) and 3H-naphtho[2,1-b]pyran (3H-NPT)) silylation by a microwave-assisted reaction between hydroxyl-substituted NPTs and 3-(triethoxysilyl)propyl isocyanate, followed by (ii) covalent post-grafting onto SiO2 NPs. In order to study the role of the silylation step, the analogous non-silylated nanomaterials were also prepared by direct adsorption of NPTs. The characterization techniques confirmed the successful NPTs silylation and subsequent grafting to SiO2 NPs. All SiO2-based nanomaterials revealed photoswitching behavior, following a biexponential decay. The SiO2 NPs functionalized with silylated 3H-NPTs (SiO2@S3 and SiO2@S4) presented the most promising photochromic properties, showing fast coloration/decoloration kinetics (coloring in 1 min under UV irradiation and fading in only 2 min) and high values of total color difference (ΔE\*ab = 30–50). Also, the 2H-NPTs-based SiO2 NPs (SiO2@S1 and SiO2@S2) presented fast coloration and good color contrasts (ΔE\*ab = 54), but slower fading kinetic rates, taking more than 2 h to return to their initial color. In contrast, the SiO2 NPs functionalized with non-silylated NPTs (SiO2@1 and SiO2@3) showed weaker color contrasts (ΔE\*ab = 6–10) and slower fading kinetics, proving that the NPT silylation step was crucial to enhance the photochromic behavior of SiO2 NPs based on NPTs. Furthermore, the silylated-based nanomaterials showed good photostability upon prolonged UV light exposure, keeping their photochromic performance unchanged for at least 12 successive UV/dark cycles, anticipating interesting technological applications in several areas.

# Naphthopyran-Based Silica Nanoparticles as New High-Performance Photoresponsive Materials\_2016

# Photostability, Electrochemistry, and Monolayers of [M(bpy)2(trans-1,2-bis(4-pyridyl)ethylene)L]+ (M = Ru, Os; L = Cl, H2O)\_2000

The development of new highly sensitive and selective methods for microarray-based analysis is a great challenge because, for many bioassays, the amount of genetic material available for analysis is extremely limited. Currently, imaging and detection of DNA microarrays are based primarily on the use of organic dyes. To overcome the problems of photobleaching and low signal intensities of organic dyes, we developed a new class of silica core−shell nanoparticles that encapsulated with cyanine dyes and applied the dye-doped nanoparticles as labeling in the DNA microarray-based bioanalysis. The developed nanoparticles have core−shell structure containing 15-nm Au colloidal cores with 95 dye−alkanethiol (dT)20 oligomers chemisorbed on the each Au particle surface and 10−15-nm silica coatings bearing thiol functional groups. To be utilized for microarray detection, the dye-doped nanoparticles were conjugated with DNA signaling probes by using heterobifunctional cross-linker. The prepared nanoparticle conjugates are stable in both aqueous electrolytes and organic solvents. Two-color DNA microarray-based detection was demonstrated in this work by using Cy3- and Cy5-doped nanoparticles in sandwich hybridization. The use of the fluorophore-doped nanoparticles in high-throughput microarray detection reveals higher sensitivity with a detection limit of 1 pM for target DNA in sandwich hybridization and greater photostable signals than the direct use of organic fluorophore as labeling. A wide dynamic range of ∼4 orders of magnitude was also found when the dye-doped nanoparticles were applied in microarray-based DNA bioanalysis. In addition, the use of these dye-doped nanoparticles as the labeling in hybridization also improved the differentiation of single-nucleotide polymorphisms. This work offers promising prospects for applying dye-doped nanoparticles as labeling for gene profiling based on DNA microarray technology.

# Improving the Signal Sensitivity and Photostability of DNA Hybridizations on Microarrays by Using Dye-Doped Core−Shell Silica Nanoparticles\_2004

The botanical insecticide azadirachtin was incorporated in alginate-based granules to obtain controlled release formulations (CRFs). The basic formulation [sodium alginate (1.47%) – azadirachtin (0.28%) – water] was modified by the addition of biosorbents, obtaining homogeneous hybrid hydrogels with high azadirachtin entrapment efficiency. The effect on azadirachtin release rate caused by the incorporation of biosorbents such as lignin, humic acid, and olive pomace in alginate formulation was studied by immersion of the granules in water under static conditions. The addition of the biosorbents to the basic alginate formulation reduces the rate of release because the lignin-based formulation produces a slower release. Photodegradation experiments showed the potential of the prepared formulations in protecting azadirachtin against simulated sunlight, thus improving its stability. The results showed that formulation prepared with lignin provided extended protection. Therefore, this study provides a new procedure to encapsulate the botanical insecticide azadirachtin, improving its delivery and photostability.

# Preparation and Characterization of Azadirachtin Alginate-Biosorbent Based Formulations: Water Release Kinetics and Photodegradation Study\_2015

Lipid droplets (LDs), as dynamic complex organelles, are involved in various physiological processes, and their numbers and activity are related to many diseases, even cancer. Hence, locating and concentration monitoring of LDs are very important to scientific bioresearch and health care. In this work, we prepared two simple luminogens (FAS and DPAS) via very facile synthetic procedures and purification. They feature aggregation-induced emission and excited state intramolecular proton transfer characteristics. They exhibit large Stokes shifts and bright orange and yellow emissions in the aggregated state, and the emissions can be reversibly turned “off” and “on” for many cycles by controlling buffer pH values. Both FAS and DPAS are cytocompatible and can selectively accumulate in and light up the LDs in living cells with superior resolution and high contrast. They also outperform the commercial LD probes in terms of photostability. Combining the advantages of high LD-specificity, good biocompatibility, surperb photostability, and low preparation cost, FAS and DPAS may become powerful tools to the study on LDs-related intracellular activities, such as LDs-based pathology and pharmacology.

# Specific Fluorescence Probes for Lipid Droplets Based on Simple AIEgens\_2016

Coenzyme Q10 (CoQ10) is widely used in preventive or curative treatment of cardiovascular diseases. However, CoQ10 exhibits an extremely low solubility in aqueous medium as well as a poor oral bioavailability. Therefore, solanesyl poly(ethylene glycol) succinate (SPGS) and CoQ10 were formulated as CoQ10-SPGS micelles with a high content of CoQ10 to improve the bioavailability of CoQ10 in rat. Findings indicate that, in the CoQ10-SPGS micelles, SPGS is self-assembled into stable nanosized micelles with a CoQ10 loading capacity of more than 39%. The CoQ10-SPGS micelles exhibit an enhanced photostability upon exposure to simulated sunlight. In vivo experiments demonstrate that, as compared to that of the coarse suspensions of CoQ10, there was three-fold enhancement of oral bioavailability for CoQ10-loaded SPGS micelles depending on varying molecular weight of SPGS. In the encapsulation of CoQ10 by SPGS micelles, the self-assembled nanocarriers with strong muco-adhesive properties lead to increases in the solubility and oral absorption of lipophilic CoQ10 nanoparticles.

# PEGylated Solanesol for Oral Delivery of Coenzyme Q10\_2017

Solution-processed ZnO sol–gel or nanoparticles are widely used as the electron-transporting layer (ETL) in optoelectronic devices. However, chemisorbed oxygen on the ZnO layer surface has been shown to be detrimental for the device performance as well as stability. Herein, we demonstrate that chemisorbed oxygen removal based on UV illumination of the ZnO surface layer under a nitrogen atmosphere can, simultaneously, improve the power conversion efficiency and photostability of PTB7-Th:PC71BM-based inverted polymer solar cells. By a systematic study of such a UV illumination procedure, we obtained optimal conditions where both the cell efficiency and stability were improved. We fabricated cells with a power conversion efficiency higher than 9.8% and with a T80 lifetime longer than 500 h, corresponding to about a 2.5-fold enhancement relative to non-UV-treated ZnO reference devices.

# UV-Induced Oxygen Removal for Photostable, High-Efficiency PTB7-Th:PC71BM Photovoltaic Cells\_2016

In this work, we investigate general mechanistic principles that control reaction selectivity following S1/S0 internal conversion in benzene. A systematic relationship is drawn between the varying topology of an extended seam of conical intersection and the balance between two competitive radiationless decay channels: photophysical (benzene reactant regeneration) and photochemical (prefulvene product formation). This is supported by a model quantum dynamics study, using a direct dynamics approach based on variational multiconfiguration Gaussian wavepackets, where initial excitation of specific vibrational modes is designed to generate dynamical pathways that reach selected targets regions of the seam. High-energy regions of the seam are found to be sloped and in favor of the photophysical channel, while lower-energy regions are peaked and give access to the photochemical channel. This changeover could in principle be exploited to define targets for optimal control, by exciting different combinations of specific vibronic levels in S1, accessing different regions of the seam, and giving different products.

# Controlling S1/S0 Decay and the Balance between Photochemistry and Photostability in Benzene: A Direct Quantum Dynamics Study\_2008

The ubiquitous nature of 1πσ\* states in biological molecules has been a prime focus in recent years. Understanding the role of this dissociative state in the amino acids and their respective chromophores following UV excitation would enable a step change toward establishing a better understanding of the mechanisms of photostability of larger peptides in the gas-phase. This letter presents the first evidence of the active involvement of 1πσ\* states in the H-atom elimination of the amino acid tyrosine and its subunit tyramine, following excitation at 200 nm.

# Active Participation of 1πσ\* States in the Photodissociation of Tyrosine and Its Subunits\_2010

Photolyses of three herbicides, bentazon, clopyralid, and triclopyr, were studied on plant leaves after crop treatment. The experiments were carried out on cuticular wax films, which are good models for leaf surfaces. The pure compounds and their commercial formulations were investigated under simulated solar light. At the recommended agricultural application rates, the three formulated herbicides photolyzed more rapidly on films than on soil or in water. Their photolysis is likely to be an important dissipation path from crops after treatment. The effects induced by the adjuvants in formulations were varied. Adjuvants slowed the photodegradation of bentazon slightly. In Garlon, in which triclopyr and clopyralid are combined, the adjuvants did not affect the photolysis of clopyralid even though they accelerated the rate of photolysis of triclopyr by a factor of 7. The kinetics were also affected by the application rates. This work also underscores the importance of assessing the photoreactivity of active ingredients in conditions similar to those of their application.

# Photodegradation of Bentazon, Clopyralid, and Triclopyr on Model Leaves: Importance of a Systematic Evaluation of Pesticide Photostability on Crops\_2009

High-performance photovoltaic polymers bearing cross-linkable function together with a photorobust conjugated backbone are highly desirable for organic solar cells to achieve both high device efficiency and long-term stability. In this study, a family of such polymers is reported based on poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c]-[1,2,5]thiadiazole)] (PPDT2FBT), a high-performance photovoltaic donor–acceptor polymer, with different contents of terminal vinyl-appended side chains for cross-linking. The polymers were named PPDT2FBT-Vx and prepared by varying the feeding ratio (x mol %, x = 0, 5, 10, and 15) of the vinyl-appended monomer in polymerization. It was found that the vinyl integration did not sacrifice the original high photovoltaic performance of the polymers, as evidenced by comparable average power conversion efficiencies (PCEs) (6.95, 7.02, and 7.63%) observed for optimized devices based on PPDT2FBT-V0, PPDT2FBT-V5, and PPDT2FBT-V10, respectively, in blending with [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM). Unlike thermal cross-linking that greatly reduced device efficiency, UV cross-linking has proven to be an effective way to achieve both high device efficiency and thermostability for PPDT2FBT-V10 solar cells. UV-cross-linked PPDT2FBT-V10 solar cells displayed an initial average PCE of 5.28% and almost no decrease upon heat treatment at 120 °C for 40 h. Morphology studies revealed that UV-cross-linking did not only alter initial nanophase separation but also suppressed morphology evolution by aggregation in bulk heterojunction blend films. Photo-cross-linking requires material photostability. It is therefore worthwhile to note that these polymers and their blends with PC71BM were found to be extremely photostable, even upon continuous exposure to concentrated sunlight (up to 200 suns), and UV-cross-linking does not hamper this photostability. Further studies found that the devices fabricated with the UV-cross-linked PPDT2FBT-V10/PC71BM active layer can endure continuous light exposure to a solar simulator without deteriorating their performance.

# UV-Cross-linkable Donor–Acceptor Polymers Bearing a Photostable Conjugated Backbone for Efficient and Stable Organic Photovoltaics\_2018

We demonstrate ultra-air- and photostable CsPbBr3 quantum dots (QDs) by using an inorganic–organic hybrid ion pair as the capping ligand. This passivation approach to perovskite QDs yields high photoluminescence quantum yield with unprecedented operational stability in ambient conditions (60 ± 5% lab humidity) and high pump fluences, thus overcoming one of the greatest challenges impeding the development of perovskite-based applications. Due to the robustness of passivated perovskite QDs, we were able to induce ultrastable amplified spontaneous emission (ASE) in solution processed QD films not only through one photon but also through two-photon absorption processes. The latter has not been observed before in the family of perovskite materials. More importantly, passivated perovskite QD films showed remarkable photostability under continuous pulsed laser excitation in ambient conditions for at least 34 h (corresponds to 1.2 × 108 laser shots), substantially exceeding the stability of other colloidal QD systems in which ASE has been observed.

# Air-Stable Surface-Passivated Perovskite Quantum Dots for Ultra-Robust, Single- and Two-Photon-Induced Amplified Spontaneous Emission\_2015

Five types of industrial lignin are blended with a pure cream and a commercial sunscreen lotion. Lignin is found to significantly boost their sunscreen performance. Photostability of the lignin-modified lotions is analyzed. The results show that hydrophobic lignin has better sunscreen performance than hydrophilic counterpart. Sun protection factor (SPF) of the pure cream containing 10% organosolv lignin (OL) reaches 8.66. Small amount of hydrophobic lignin dramatically increases SPF value of the sunscreen lotions. Adding 1% lignin almost doubles the sun lotion’s SPF. Addition of 10% OL to the lotion boosts its SPF from 15 to 91.61. However, it is also found that hydrophilic lignin tends to demulsify the lotions due to an electrostatic disequilibrium. After 2 h of UV radiation, UV absorbance of all the five lignin-modified sunscreen lotions increases up to the limit of measuring instrument. All the lignin types studied in this work are found to have a general synergistic effect with sunscreen actives in the commercial lotion. An effort is also made to elucidate radical mechanisms of the synergy.

# Sunscreen Performance of Lignin from Different Technical Resources and Their General Synergistic Effect with Synthetic Sunscreens\_2016

CdS has been regarded as a promising photocatalytic water-splitting visible-light photocatalyst, but low catalytic activity and photocorrosion seriously limited its practical application. Here, inspired by core–shell principles, we try to fabricate CdS@MoS2 core–shell structures by utilizing unstable CdS nanowires as core and multilayered MoS2 as shell. Multilayered MoS2 not only serves as a protective shell to preserve CdS but also provides abundant reactive sites and forms a type I junction, giving rise to remarkable hydrogen production activities. The optimum hydrogen production rate based on CdS@MoS2 core–shell composite reaches 26.14 mmol·h–1·g–1, which is about 54 times greater than that of pure CdS and about twice that of CdS nanowires with 1% Pt. Impressively, the presentation of MoS2 nanosheets can effectively avoid photocorrosion, which resulted in 12 h stable hydrogen production.

# Simultaneous Realization of Enhanced Photoactivity and Promoted Photostability by Multilayered MoS2 Coating on CdS Nanowire Structure via Compact Coating Methodology\_2017

Organic–inorganic hybrid lead halide perovskites have recently realized significant development. However, the toxicity of lead (Pb) and the poor stability might eventually hamper the commercialization of perovskite solar cells (PSCs). Here, we present an environment friendly and stable all inorganic rudorffite AgBiI4 as solar absorber by solution-based synthesis of thin-films. AgBiI4 films fabricated by 0.6 M solution and annealed at 150 °C show dense grains and high surface coverage. Furthermore, the AgBiI4 films exhibit greater thermal stability and photostability than CH3NH3PbI3. Ultimately, by judiciously choosing the hole transport material with appropriate energy level, the solar cell device demonstrates high carrier extraction efficiency and achieve a power conversion efficiency (PCE) of 2.1% under standard 1 sun (AM 1.5). The devices also show excellent long-term air stability and still maintain 96% of its initial PCE even after 1000h at relative humidity of 26%. This work highlights new directions for further exploration of Pb-free and stable solar cells.

# Inorganic and Lead-Free AgBiI4 Rudorffite for Stable Solar Cell Applications\_2018

In recent years, lead halide perovskite nanocrystals (NCs) have attracted significant attention in both fundamental research and commercial applications because of their excellent optical and optoelectrical properties. However, the protective ligands on the surface of the perovskite NCs could be easily removed after the tedious process of centrifugation, separation, and dispersion, which greatly hampers their stability against light, heat, moisture, and oxygen and limits their practical applications. Here, we report a new post-processing free strategy (i.e., without centrifugation, separation, and dispersion process) of using an ultraviolet (UV)-polymerizable acrylic monomer of lauryl methacrylate as the solvent to synthesize CsPbBr3 NCs, and then adding polyester polyurethane acrylate oligomer, monomer (IBOA), and initiator for direct UV polymerization to fabricate NC–polymer composite films. These films exhibited an improved photoluminescence quantum yield (85–90%) than classic NC films (40–50%), which were processed using octadecene (ODE) as the solvent for NC synthesis and postprocessed for UV polymerization. Significantly, the as-fabricated films by post-processing free strategy exhibited excellent photostability against strong Xe lamp illumination; while the other films using classic methods were quickly photodegraded. Meanwhile, these NC–polymer composite films showed good stability against moisture and heating when aging in water at 50 °C for over 200 h. These films, along with K2SiF6:Mn4+ (KSF) phosphor emitters, were used as downconverters for blue light-emitting diodes in liquid-crystal displays with a wide color gamut of 115% in the International Commission on Illumination (CIE) 1931 color space. This work provides a facile and effective strategy for the preparation of ultrastable and bright color-conversion NC films for the development of the next-generation wide color gamut displays.

# Direct Hot-Injection Synthesis of Lead Halide Perovskite Nanocubes in Acrylic Monomers for Ultrastable and Bright Nanocrystal–Polymer Composite Films\_2019

Highly efficient blue-emitting CdSe-derived core/shell gradient alloy quantum dots (CSGA QDs) with photoluminescence quantum yield (PL QY) of ca. 90% have been synthesized through a facile “one-pot” approach. CdSe nuclei are initially formed as core and gradient alloy shells such as CdSexS1–x/ZnSeyS1–y simultaneously encapsulate the preformed CdSe core in an energy-gradient fashion eventually followed by coating with ZnS shells due to the faster precursor reaction kinetics of Cd and Se compared to analog of Zn and S. During the formation of core/shell structure, red-shifting of absorption/emission peaks followed by blue-shifting of analogues were observed due to the intradiffusion of sulfur anion to CdSe luminescent center. In this gradient architecture, interfacial lattice strain can be effectively alleviated, and thus high PL QY (ca. 90%) and enhanced photochemical stability can be achieved. The synthesized blue-emitting gradient alloy QDs with superior optical properties tunable in the range of 450–490 nm can be used for highly efficient blue-emitters and potentially applicable for the fabrication of white-light LEDs.

# Highly efficient Blue-Emitting CdSe-derived Core/Shell Gradient Alloy Quantum Dots with Improved Photoluminescent Quantum Yield and Enhanced Photostability\_2017

Highly fluorescent copper nanoclusters (Cu NCs) have been synthesized using single-step reduction of copper sulfate by hydrazine in the presence of lysozyme. The fluorescence quantum yield was measured to be as high as 18%. The emission was also found to be dependent on the excitation wavelength. Mass spectrometric analyses indicated the presence of species corresponding to Cu2 to Cu9. Transmission electron microscopic analyses indicated the formation of agglomerated particles of average diameter of 2.3 nm, which were constituted of smaller particles of average diameter of 0.96 nm. They were found to be stable between pH 4 and 10 and in addition having excellent chemical and photostability. The noncytotoxic NCs were used to successfully label cervical cancer HeLa cells.

# Blue-Emitting Copper Nanoclusters Synthesized in the Presence of Lysozyme as Candidates for Cell Labeling\_2014

In this study, nine pyrimethanil ionic liquids (PILs) were synthesized through an acid–base reaction with nine naturally derived organic acid anions to improve the physicochemical properties and reduce the environmental adverse impacts. The PILs presented lower volatilization, higher photostability, better soil adsorption capacity, and improved fungicidal activity relative to pyrimethanil. When the length of the carbon chains in the anions was increased, the PILs showed better properties in terms of melting point, water solubility, volatility, and surface tension. The photostabilities and fungicidal activities of the PILs were significantly improved when cyclic compounds were used as the paired anion ions. With enhanced physicochemical properties and better fungicidal activity, PIL7 was selected as the best alternative to pyrimethanil. The intrinsic disadvantages of pyrimethanil could be surmounted using the system developed in the study; thus, ILs could have immense potential in the development of eco-friendly and efficient fungicides in the future.

# Pyrimethanil Ionic Liquids Paired with Various Natural Organic Acid Anions for Reducing Its Adverse Impacts on the Environment\_2019

Doubly and triply linked porphyrin−perylene monoimides 3 and 4, with extraordinary stability, large dipole moments, and strong near IR absorption, were prepared by means of one-pot oxidative cyclodehydrogenation promoted by FeCl3.

# Doubly and Triply Linked Porphyrin−Perylene Monoimides as Near IR Dyes with Large Dipole Moments and High Photostability\_2010

Although oxide nanowires offer advantages for next-generation transparent display applications, they are also one of the most challenging materials for this purpose. Exposure of semiconducting channel areas of oxide nanowire transistors produces an undesirable increase in the photocurrent, which may result in unstable device operation. In this study, we have developed a Zn2SnO4 nanowire transistor that operates stably regardless of changes in the external illumination. In particular, after exposure to a light source of 2100 lx, the threshold voltage (Vth) showed a negative shift of less than 0.4 V, and the subthreshold slope (SS) changed by ∼0.1 V/dec. ZnO or SnO2 nanowire transistors, in contrast, showed 1.5–2.0 V negative shift in Vth and an SS change of ∼0.3 V/dec under the same conditions. Furthermore, the Zn2SnO4 nanowire transistors returned to their initial state immediately after the light source was turned off, unlike those using the other two nanowires. Thus, Zn2SnO4 nanowires achieve photostability without the application of a black material or additional processing, minimizing the photocurrent effect for display devices.

# Photostable Zn2SnO4 Nanowire Transistors for Transparent Displays\_2012

Avermectin (AVM) is a low-toxic and high-active biopesticide, but it can be easily degraded by UV light. In this paper, biodegradable castor oil-based polyurethanes (CO-PU) are synthesized and used as carriers to fabricate a new kind of AVM/CO-PU nanoemulsion through an emulsion solvent evaporation method, and the chemical structure, colloidal property, AVM loading capacity, controlled-release behavior, foliar adhesion, and photostability of the AVM/CO-PU drug delivery systems are investigated. Results show that AVM is physically encapsulated in the CO-PU carrier nanospheres, the diameter of the AVM/CO-PU nanoparticles is <50 nm, and the AVM/CO-PU films are flat and smooth without any AVM aggregate. The drug loading capacity is up to 42.3 wt % with a high encapsulation efficiency of >85%. The release profiles indicate that the release rate is relatively high at the early stage and then slows, which can be adjusted by loaded AVM content, temperature, and pH of the release medium. The foliar pesticide retention of the AVM/CO-PU nanoemulsions is improved, and the photolysis rate of AVM in the AVM/CO-PU nanoparticles is significantly slower than that of the free AVM. A release mechanism of the AVM/CO-PU nanoemulsions is proposed, which is controlled by both diffusion and matrix erosion.

# Preparation and Characterization of Controlled-Release Avermectin/Castor Oil-Based Polyurethane Nanoemulsions\_2017

We introduce new oxygen- and moisture-proof polymer matrixes based on polyisobutylene (PIB) and its block copolymer with styrene [poly(styrene-block-isobutylene-block-styrene), PSt-b-PIB-b-PSt] for the encapsulation of colloidal semiconductor nanocrystals. In order to prepare transparent and processable composites, we developed a special procedure of nanocrystal surface engineering including ligand exchange of parental organic ligands to inorganic species followed by the attachment of specially designed short-chain PIB functionalized with an amino group. The latter provides excellent compatibility of the particles with the polymer matrixes. As colloidal nanocrystals, we chose CdSe nanoplatelets (NPLs) because they possess a large surface and thus are very sensitive to the environment, in particular in terms of their limited photostability. The encapsulation strategy is quite general and can be applied to a wide variety of semiconductor nanocrystals, as demonstrated on the example of PbS quantum dots. All obtained composites exhibited excellent photostability, being tested in a focus of a powerful white-light source, as well as exceptional chemical stability in a strongly acidic media. We compared these properties of the new composites with those of widely used polyacrylate-based materials, demonstrating the superiority of the former. The developed composites are of particular interest for application in optoelectronic devices, such as color-conversion light-emitting diodes, laser diodes, luminescent solar concentrators, etc.

# Robust Polymer Matrix Based on Isobutylene (Co)polymers for Efficient Encapsulation of Colloidal Semiconductor Nanocrystals\_2019

CsPbX3 (X = Cl, Br, I) perovskite quantum dots (PQDs) have been intensively investigated on photoelectric devices due to their superior optical properties. To date, the stability of CsPbX3 PQDs is still an open challenge. The previous mixed-halide CsPbX3 PQDs were generally obtained via the anion-exchange method at 40 °C. Here, the single- and mixed-halide CsPbX3 PQDs are synthesized at high temperature via the hot injection technique. The surface ligands could thus be strongly coordinated onto the surface of the PQDs, which dramatically improve the optical properties of the PQDs. The resulting CsPbX3 PQDs have high quantum yield (QY, 40–95%), narrow full width at half-maximum (FWHM) (the narrowest FWHM <10 nm), tunable band gap (408–694 nm), and highly strong photostability. The variation of their emission peaks upon anion atoms is well-supported by the theoretical band gaps calculated by the density functional theory calculations with the alloy formula correction. Hence, these PQDs show great potential as good candidates for photoelectric devices.

# Highly Controllable and Efficient Synthesis of Mixed-Halide CsPbX3 (X = Cl, Br, I) Perovskite QDs toward the Tunability of Entire Visible Light\_2017

Controlling the photostability of the organometallic complex is vital for obtaining the long-lasting phosphorescent organic light-emitting diode. In this article, the density functional theory was employed to investigate the photostabilities of a series of tridentate Pt(II) complexes in the triplet–triplet annihilation (TTA) processes. The calculated results indicate that the existence of the Pt–C\*(NHC) bond can increase the Gibbs free main ligand dissociation energy to avoid the main ligand dissociation during the TTA process. According to the Wiberg bond order and electron localization function, the positive effect of the Pt–C\*(NHC) bond originates from the strong d and p orbital interactions and more electron localization between C\*(NHC) and Pt atoms. In addition, the study in this article also manifests that the auxiliary ligands with strong electron-withdrawing/-donating properties can facilitate the electron localization, leading to the increase of photostabilities for the tridentate Pt(II) complexes. These results are useful and valuable for controlling the photostabilities of tridentate Pt(II) complexes and designing the stable blue Pt(II) complexes.

# Strategy Used for Controlling the Photostability of Tridentate Pt(II) Complexes To Enhance the Device Lifetimes of Blue Phosphorescent Organic Light-Emitting Diodes: The Role of the Pt-C\*(NHC) Bond and Auxiliary Ligand\_2018

A novel near-infrared-responsive (NIR-responsive) photothermal therapy (PTT) agent based on perylene-diimide-encapsulated (PDI-encapsulated) PEGylated silica nanocapsules (SNCs) is developed. Dicyclohexylamino-PDI (DCAPDI) with electron-donating cyclohexylamino substitutes at bay positions aggregates into J-aggregation in the core of SNCs, and their electronic coupling interactions are strengthened because of the spatial confinement of SNCs, resulting in strong NIR absorption but negligible fluorescence emission which is crucial for NIR-responsive PTT. Based on our knowledge, this is the first example of generating NIR photothermal conversion by means of molecular aggregation derived from spatial confinement. Unprecedented photostability is achieved with the DCAPDI-encapsulated SNCs in response to more than 60 runs of cyclic NIR exposure with each run exposed to the 808 nm, 1 W cm–2 laser for 10 min. It overcomes the common photodegradation problem of small organic NIR dyes under continuous high-power laser irradiation thanks to the robust molecular skeleton of PDIs and their formation of structurally stable J-aggregates in SNCs. The DCAPDI-encapsulated SNCs demonstrate low cellular cytotoxicity and excellent in vivo photothermal efficacy in tumor ablation in a tumor-bearing zebrafish model, and thus allow the practical employment of a stable photothermal agent in clinical applications.

# J-Aggregation of Perylene Diimides in Silica Nanocapsules for Stable Near-Infrared Photothermal Conversion\_2019

# Excited state chemistry of indigoid dyes. II. Interaction of thio- and selenoindigo dyes with hydroxylic compounds and its implications on the photostability of indigo\_1973

# Toward the Photostability Mechanism of Intramolecular Hydrogen Bond Systems. 4. 3(5)-(1'-Hydroxy-2'-naphthyl)pyrazoles and 3(5)-(2'-Hydroxy-1'-naphthyl)pyrazoles\_1995

Indoline photosensitizers exhibit impressive short-circuit photocurrent but generally low molar extinction coefficient and rapid charge recombination, which limits their application in thin-film dye-sensitizerd solar cells (DSCs). Here, we incorporate a new dithieno[3,2-b:2′,3′-d]pyrrole (DTP) segment (i.e., dihexyloxy-triphenylamine (DHO-TPA) substituted DTP) as the conjugated π-linker to construct a series of high molar absorption coefficient indoline dyes (XW69, XW70, and XW71) for DSCs employing a cobalt(II/III) redox electrolyte. Interestingly, this DTP linker is demonstrated as an efficient building block, not only slowing down the kinetics of charge recombination of titania electrons with tris(1,10-phenanthroline)cobalt(III) ions but also making a great contribution to the light absorption properties in comparison with the dihexylaniline substituted DTP. With respect to the dihexyloxy-triphenylamine dye (XW68), these new indoline dyes exhibit stronger light-harvesting and thus better power conversion efficiency of DSCs made from thin titania films. Benefitting from the bulky rigidity of the donor and π-conjugation unit, the XW70 dye displays a promising conversion efficiency as high as 8.78%, with a short-circuit current density (JSC) of 13.3 mA cm–2, open-circuit voltage (VOC) of 943 mV, and fill factor (FF) of 0.70 under AM 1.5 illumination (100 mW cm–2). Furthermore, the effect of light irradiation on these dyes adsorbed on nanocrystalline TiO2 films was investigated, proving the photostability of these indoline chromophores. Our work has valued the feasibility of judicious design of indoline chromophores to obtain organic photosensitizers for high-efficiency iodine-free DSCs made from thin titania films.

# Judicious Design of Indoline Chromophores for High-Efficiency Iodine-Free Dye-Sensitized Solar Cells\_2014

Biodegradable and renewable UV-shielding films are highly demanded to meet the increasing sustainable requirement for the environment. Lignin as a natural broad UV blocker has gained considerable attention; however, the poor dispersibility within synthetic polymers limited its applications. Thus, a bioinspired melanin-like polydopamine thin layer was incorporated for the first time with lignin nanoparticle (LNP) in this effort, forming a UV-blocking core–shell lignin–melanin nanoparticle (LMNP) with higher compatibility and durability. Subsequently, LNP, LMNP, melanin nanoparticles (MNP), and a mix of LNP and MNP (MixNP) were compounded with poly(butylene adipate-co-terephthalate) (PBAT), to enhance the UV-barrier capability and photostability of PBAT films. The incorporated LMNPs were well distributed into PBAT, leading to improved tensile properties and thermal stability of the resulting films. All these films possessed remarkable UV-blocking capacity at NP concentration ranging from 0.5 to 5 wt %, blocking almost all of UV-A and more than 80% of UV-B light, while an appreciable optical transmittance could also be achieved. The PBAT–LMNP films displayed a high UV-shielding stability and the best retention in mechanical properties after UV exposure for 40 h. This work provides a very promising approach for fabricating biodegradable PBAT-based UV-blocking films for potential applications in agricultural or food packaging materials where the UV resistance is highly required.

# Biodegradable UV-Blocking Films through Core–Shell Lignin–Melanin Nanoparticles in Poly(butylene adipate-co-terephthalate)\_2019

The development of a suitable fluorescent probe for the specific labeling and imaging of lysosomes through the direct visual fluorescent signal is extremely important for understanding the dysfunction of lysosomes, which might induce various pathologies, including neurodegenerative diseases, cancer, and Alzheimer’s disease. Herein, a new carbon dot-based fluorescent probe (CDs-PEI-ML) was designed and synthesized for highly selective imaging of lysosomes in live cells. In this probe, PEI (polyethylenimine) is introduced to improve water solubility and provide abundant amine groups for the as-prepared CDs-PEI, and the morpholine group (ML) serves as a targeting unit for lysosomes. More importantly, passivation with PEI could dramatically increase the fluorescence quantum yield of CDs-PEI-ML as well as their stability in fluorescence emission under different excitation wavelength. Consequently, experimental data demonstrated that the target probe CDs-PEI-ML has low cytotoxicity and excellent photostability. Additionally, further live cell imaging experiment indicated that CDs-PEI-ML is a highly selective fluorescent probe for lysosomes. We speculate the mechanism for selective staining of lysosomes that CDs-PEI-ML was initially taken up by lysosomes through the endocytic pathway and then accumulated in acidic lysosomes. It is notable that there was less diffusion of CDs-PEI-ML into cytoplasm, which could be ascribed to the presence of lysosome target group morpholine on surface of CDs-PEI-ML. The blue emission wavelength combined with the high photo stability and ability of long-lasting cell imaging makes CDs-PEI-ML become an alternative fluorescent probe for multicolor labeling and long-term tracking of lysosomes in live cells and the potential application in super-resolution imaging. To best of our knowledge, there are still limited carbon dots-based fluorescent probes that have been studied for specific lysosomal imaging in live cells. The concept of surface functionality of carbon dots will also pave a new avenue for developing carbon dots-based fluorescent probes for subcellular labeling.

# Morpholine Derivative-Functionalized Carbon Dots-Based Fluorescent Probe for Highly Selective Lysosomal Imaging in Living Cells\_2017

Colloidal quantum dots (QDs) of lead halide perovskite have recently received great attention owing to their remarkable performances in optoelectronic applications. However, their wide applications are hindered from toxic lead element, which is not environment- and consumer-friendly. Herein, we utilized heterovalent substitution of divalent lead (Pb2+) with trivalent antimony (Sb3+) to synthesize stable and brightly luminescent Cs3Sb2Br9 QDs. The lead-free, full-inorganic QDs were fabricated by a modified ligand-assisted reprecipitation strategy. A photoluminescence quantum yield (PLQY) was determined to be 46% at 410 nm, which was superior to that of other reported halide perovskite QDs. The PL enhancement mechanism was unraveled by surface composition derived quantum-well band structure and their large exciton binding energy. The Br-rich surface and the observed 530 meV exciton binding energy were proposed to guarantee the efficient radiative recombination. In addition, we can also tune the inorganic perovskite QD (Cs3Sb2X9) emission wavelength from 370 to 560 nm via anion exchange reactions. The developed full-inorganic lead-free Sb-perovskite QDs with high PLQY and stable emission promise great potential for efficient emission candidates.

# High Quantum Yield Blue Emission from Lead-Free Inorganic Antimony Halide Perovskite Colloidal Quantum Dots\_2017

We synthesized a series of push–pull-type copolymers by copolymerizing an electron-deficient diketopyrrolopyrrole with three electron-donating benzodithiophene (BDT) moieties. PDPPDTT, which incorporated a dithienothiophene (DTT), showed a higher power conversion efficiency (PCE) of 6.11% compared to 3.31% for the BDT-based polymer (PDPPBDT). PDPPDTBDT, which incorporated a dithienobenzodithiophene (DTBDT), also exhibited superior performance, with a PCE of 4.75% although this value was lower than that obtained for PDPPDTT. The presence of the DTT unit in the polymer backbone lowered the energy bandgap of the polymer and induced an optimal morphology in the polymer:PC71BM blend film, resulting in higher charge carrier generation. Furthermore, the effectively delocalized frontier orbitals of PDPPDTT enhanced intermolecular interactions between the polymer chains by favoring effective π–π stacking, which facilitated charge carrier transport. By contrast, PDPPDTBDT unexpectedly showed a low-crystallinity thin film despite its backbone planarity, which reduced the performance relative to that of PDPPDTT. Importantly, PDPPDTT exhibited significantly better device stability compared to the other polymers in a light soaking test due to the much higher photochemical stability of PDPPDTT. We demonstrated a systematic approach to simultaneously increasing the photovoltaic performances and device stability, and we explored the basis for the structure–property relationship that accompanied such improvements.

# Simultaneous Enhancement of Solar Cell Efficiency and Photostability via Chemical Tuning of Electron Donating Units in Diketopyrrolopyrrole-Based Push–Pull Type Polymers\_2014

Despite the extensive investigations thus far, there is still debate regarding the role of the repulsive πσ\* state in the photochemistry of adenine. We present evidence that suggests that H-atom elimination via both the azole group (N9) and the often overlooked amino group (N6) occurs following excitation at 200 nm. In contrast, excitation at 266 nm supports the view that the role of the πσ\* states is minimal.

# Competing πσ\* States in the Photodissociation of Adenine\_2010

We report a designed strategy for a synthesis of highly luminescent and photostable composites by incorporating quantum dots (QDs) into layered double hydroxide (LDH) matrices without deterioration of a photoluminescence (PL) efficiency of the fluorophores during the entire processes of composite formations. The QDs synthesized in an organic solvent are encapsulated by polymers, poly(maleic acid-alt-octadecene) to transfer them into water without altering the initial surface ligands. The polymer-encapsulated QDs with negative zeta potentials (−29.5 ± 2.2 mV) were electrostatically assembled with positively charged (24.9 ± 0.6 mV) LDH nanosheets to form QD-polymer-LDH composites (PL quantum yield: 74.1%). QD-polymer-LDH composite films are fabricated by a drop-casting of the solution on substrates. The PL properties of the films preserve those of the organic QD solutions. We also demonstrate that the formation of the QD-polymer-LDH composites affords enhanced photostabilities through multiple protections of QD surface by polymers and LDH nanosheets from the environment.

# Highly Fluorescent and Stable Quantum Dot-Polymer-Layered Double Hydroxide Composites\_2013

2-Aminooxazole has recently been proposed as a hypothetical precursor of RNA nucleotides on early earth. UV irradiation was considered as a crucial environmental factor in the proposed reaction sequence. We report on state-of-the-art multireference quantum-chemical calculations elucidating the possible nonradiative deactivation channels of this compound. According to our findings, the gas-phase photochemistry of 2-aminooxazole should be dominated by the photodetachment of the hydrogen atom of the NH2 group via a 1πσNH\* state leading either to ultrafast nonradiative deactivation, phototautomerization, or photodissociation of a hydrogen atom. We also identified a possible ring-opening reaction and a ring-puckering process that could occur after electronic excitation. These reactions seem to be less probable because they are driven by a higher-lying excited singlet state and are inherently slower than the hydrogen-atom dynamics.

# Drugs:  Photochemistry and Photostability Edited by A. Albini and E. Fasani (Dell' Universita Di Pavia). Royal Society of Chemistry:  Cambridge. 1998. viii + 330 pp. ISBN 0-85404-743-3.\_1999

Fluorescent nanoparticles with optically robust luminescence are imperative to applications in imaging and labeling. Here we demonstrate that hexagonal boron nitride (hBN) nanoparticles can be reliably produced using a scalable cryogenic exfoliation technique with sizes below 10 nm. The particles exhibit bright fluorescence generated by color centers that act as atomic-size quantum emitters. We analyze their optical properties, including emission wavelength, photon-statistics, and photodynamics, and show that they are suitable for far-field super-resolution fluorescence nanoscopy. Our results provide a foundation for exploration of hBN nanoparticles as candidates for bioimaging, labeling, as well as biomarkers that are suitable for quantum sensing.

# Photochemistry of 2-Aminooxazole, a Hypothetical Prebiotic Precursor of RNA Nucleotides\_2013

Engineering a compact, near-infrared plasmonic nanostructure with integrated image-enhancing agents for combined imaging and therapy is an important nanomedical challenge. Recently, we showed that Au@SiO2@Au nanomatryoshkas (NM) are a highly promising nanostructure for hosting either T1 MRI or fluorescent contrast agents with a photothermal therapeutic response in a compact geometry. Here, we show that a near-infrared-resonant NM can provide simultaneous contrast enhancement for both T1 magnetic resonance imaging (MRI) and fluorescence optical imaging (FOI) by encapsulating both types of contrast agents in the internal silica layer between the Au core and shell. We also show that this method of T1 enhancement is even more effective for Fe(III), a potentially safer contrast agent compared to Gd(III). Fe–NM-based contrast agents are found to have relaxivities 2× greater than those found in the widely used gadolinium chelate, Gd(III) DOTA, providing a practical alternative that would eliminate Gd(III) patient exposure entirely. This dual-modality nanostructure can enable not only tissue visualization with MRI but also fluorescence-based nanoparticle tracking for quantifying nanoparticle distributions in vivo, in addition to a near-infrared photothermal therapeutic response.

# Facile Production of Hexagonal Boron Nitride Nanoparticles by Cryogenic Exfoliation\_2019

The excellent intrinsic optoelectronic properties of methylammonium lead halide perovskites (MAPbX3, X = Br, I), such as high photoluminescence quantum efficiency, long carrier lifetime, and high gain coupled with the facile solution growth of nanowires make them promising new materials for ultralow-threshold nanowire lasers. However, their photo and thermal stabilities need to be improved for practical applications. Herein, we report a low-temperature solution growth of single crystal nanowires of formamidinium lead halide perovskites (FAPbX3) that feature red-shifted emission and better thermal stability compared to MAPbX3. We demonstrate optically pumped room-temperature near-infrared (∼820 nm) and green lasing (∼560 nm) from FAPbI3 (and MABr-stabilized FAPbI3) and FAPbBr3 nanowires with low lasing thresholds of several microjoules per square centimeter and high quality factors of about 1500–2300. More remarkably, the FAPbI3 and MABr-stabilized FAPbI3 nanowires display durable room-temperature lasing under ∼108 shots of sustained illumination of 402 nm pulsed laser excitation (150 fs, 250 kHz), substantially exceeding the stability of MAPbI3 (∼107 laser shots). We further demonstrate tunable nanowire lasers in wider wavelength region from FA-based lead halide perovskite alloys (FA,MA)PbI3 and (FA,MA)Pb(I,Br)3 through cation and anion substitutions. The results suggest that formamidinium lead halide perovskite nanostructures could be more promising and stable materials for the development of light-emitting diodes and continuous-wave lasers.

# Routes to Potentially Safer T1 Magnetic Resonance Imaging Contrast in a Compact Plasmonic Nanoparticle with Enhanced Fluorescence\_2018

We introduce a new class of photostable, efficient photosensitizers based on boron-dipyrromethene (BODIPY) derivatives that can generate singlet oxygen and super oxide simultaneously under irradiation. For compound preparation, appropriate regulation of the reaction conditions and control of specifically substituted BODIPY derivatives have been achieved. After biologically evaluating the intracellular uptake, localization, and phototoxicity of the compounds, we conclude that 3,5-dianiline-substituted BODIPY is a potentially selective photodynamic therapy candidate because its photodamage is more efficient in cancer cells than in normal cells, without apparent dark toxicity. Furthermore, direct comparison of photodamage efficacy revealed that our compound has better efficacy than Foscan and nearly equal efficacy to that of methylene blue.

# Nanowire Lasers of Formamidinium Lead Halide Perovskites and Their Stabilized Alloys with Improved Stability\_2016

Immunoglobulin gamma (IgG) monoclonal antibodies (mAbs) are glycoproteins that have emerged as powerful and promising protein therapeutics. During the process of production, storage and transportation, exposure to ambient light is inevitable, which can cause protein physical and chemical degradation. For mechanistic studies of photodegradation, we have exposed IgG4-Fc to UV light. The photoirradiation of IgG4-Fc with monochromatic UVC light at λ = 254 nm and UVB light with λmax = 305 nm in air-saturated solutions revealed multiple photoproducts originating from tyrosine side chain fragmentation at Tyr300, Tyr373, and Tyr436. Tyr side chain fragmentation yielded either Gly or various backbone cleavage products, including glyoxal amide derivatives. A mechanism is proposed involving intermediate Tyr radical cation formation, either through direct light absorption of Tyr or through electron transfer to an initial Trp radical cation, followed by elimination of quinone methide. Product formation showed either no (cleavage of Tyr373) or significant (cleavage of Tyr436) inverse product solvent isotope effects (SIEs), indicating a role for proton transfer in the cleavage mechanism of Tyr436. The role of electron transfer in the cleavage of Tyr436 was further investigated through mutation of an adjacent Trp381. This is the first observation of a photoinduced Tyr side chain cleavage reactions in a protein.

# Special Reactive Oxygen Species Generation by a Highly Photostable BODIPY-Based Photosensitizer for Selective Photodynamic Therapy\_2013

Metal complex-based luminescent oxygen nanosensors have been intensively studied for biomedical applications. In terms of monitoring dynamics of intracellular oxygen, however, high-quality nanosensors are still badly needed, because of stringent requirements on stability, biocompatibility and luminescence intensity, aside from oxygen sensitivity. In this paper, we reported a type of highly luminescent and stable oxygen nanosensors prepared from metallopolymer. First, a novel ruthenium(II)-containing metallopolymer was synthesized by chelating the oxygen probe [Ru(bpy)3]2+ with a bipyridine-branched hydrophobic copolymer, which was then doped into polymeric nanoparticles (NPs) by a reprecipitation method, followed by further conjugation to selectively target mitochondria (Mito-NPs). The resultant Mtio-NPs possessed a small hydrodynamic size of ∼85 nm, good biocompatibility and high stability resulting from PEGylation and stable nature of Ru-complex. Because the complexed [Ru(bpy)3]2+ homogeneously resided on particle surface, Mito-NPs exhibited strong luminescence at 608 nm that was free of aggregation-caused-quenching, the utmost oxygen sensitivity of free [Ru(bpy)3]2+ probe (Q = 75%), and linear Stern–Volmer oxygen luminescence quenching plots. Taking advantage of the mitochondria-specific nanosensors, intracellular oxygenation and deoxygenation processes were real-time monitored for 10 min by confocal luminescence imaging, visualized by the gradual weakening (by more than 90%) and enhancing (by 50%) of the red emission, respectively.

# Photoinduced Tyrosine Side Chain Fragmentation in IgG4-Fc: Mechanisms and Solvent Isotope Effects\_2018

CsPbX3 (X = Cl, Br, and I) perovskite nanocrystals (NCs) are known for their exceptional optoelectronic properties, yet the material’s instability toward polar solvents, heat, or UV irradiation greatly limits its further applications. Herein, an efficient in situ growing strategy has been developed to give highly stable perovskite NC composites (abbreviated CsPbX3@CA-SiO2) by anchoring CsPbX3 NCs onto silica nanowires (NWs), which effectively depresses the optical degradation of their photoluminescence (PL) and enhances stability. The preparation of surface-functionalized serpentine silica NWs is realized by a sol–gel process involving hydrolysis of a mixture of tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), and trimethoxy(octadecyl)silane (TMODS) in a water/oil emulsion. The serpentine NWs are formed via an anisotropic growth with lengths up to 8 μm. The free amino groups are employed as surface ligands for growing perovskite NCs, yielding distributed monodisperse NCs (∼8 nm) around the NW matrix. The emission wavelength is tunable by simple variation of the halide compositions (CsPbX3, X = Cl, Br, or I), and the composites demonstrate a high photoluminescence quantum yield (PLQY 32–69%). Additionally, we have demonstrated the composites CsPbX3@CA-SiO2 can be self-woven to form a porous 3D hierarchical NWs membrane, giving rise to a superhydrophobic surface with hierarchical micro/nano structural features. The resulting composites exhibit high stability toward water, heat, and UV irradiation. This work elucidates an effective strategy to incorporate perovskite nanocrystals onto functional matrices as multifunctional stable light sources.

# Highly Stable and Luminescent Oxygen Nanosensor Based on Ruthenium-Containing Metallopolymer for Real-Time Imaging of Intracellular Oxygenation\_2019

Mesenchymal stem cells (MSCs) have proved to be a promising and abundant cell source for tissue and organ repair in regenerative medicine. However, the cell fate, distribution and migration of these transplanted cells are still unclear due to the limited tracking methods. It is desirable to develop a biocompatible and photostable probe to label the MSCs for long-term tracking without affecting the cell proliferation and potency. Herein we apply a recently developed nanoprobe system, in which di(thiophene-2-yl)-diketopyrrolopyrrole (DPP) is covalently linked in the middle of polycaprolactone (PCL) forming the PCL-DPP-PCL polymer complex. Although the PCL-DPP-PCL nanoparticles uptaken by the MSCs did not affect the cell viability, it was interesting that they exhibited different effects on the multilineage potency of the MSCs in the subsequent differentiation in vitro. Specifically, we found that the PCL-DPP-PCL labeling was unfavorable to the MSC osteogenic differentiation, whereas the labeled MSCs exhibited the same adipogenic and chondrogenic differentiations compared to the unlabeled controls as verified by gene expressions and histological staining. Furthermore, the PCL-DPP-PCL nanoparticles remained strong fluorescence intensity even after 4 weeks of differentiation. This study indicated that PCL-DPP-PCL nanoparticles could be used for long-term cell tracing in MSC differentiation into adipogenic and chondrogenic lineages.

# Highly Stable Luminous “Snakes” from CsPbX3 Perovskite Nanocrystals Anchored on Amine-Coated Silica Nanowires\_2018

Binding functional molecules to nanostructured mesoporous metal oxide surfaces provides a way to derivatize metal oxide semiconductors for applications in dye-sensitized photoelectrosynthesis cells (DSPECs). The commonly used anchoring groups, phosphonates and carboxylates, are unstable as surface links to oxide surfaces at neutral and high pH, leading to rapid desorption of appended molecules. A synthetically versatile molecular attachment strategy based on initial surface modification with a silyl azide followed by click chemistry is described here. It has been used for the stable installation of surface-bound metal complexes. The resulting surfaces are highly stabilized toward complex loss with excellent thermal, photochemical, and electrochemical stabilities. The procedure involves binding 3-azidopropyltrimethoxysilane (APTMS) to nanostructured mesoporous TiO2 or tin-doped indium oxide (ITO) electrodes by silane attachment followed by azide-terminated, Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reactions with an alkyne-derivatized ruthenium(II) polypyridyl complex. The chromophore-modified electrodes display enhanced photochemical and electrochemical stabilities compared to phosphonate surface binding with extended photoelectrochemical oxidation of hydroquinone for more than ∼6 h with no significant decay.

# Long-Term Tracking Mesenchymal Stem Cell Differentiation with Photostable Fluorescent Nanoparticles\_2016

We report on the intriguing phenomenon of the evolution of photoluminescence from CdSe core, CdSe/ZnS core/shell, and CdSe/Cd1–xZnxSe1–ySy core/graded shell green-emitting quantum dots (QDs). The thickness and composition profile of QDs was found to control how the optical characteristics evolve under different light exposure conditions. Unexpectedly, changes of emission intensity (decreasing and increasing) and spectral band position were observed, which can be reversible or irreversible, depending on the QD architecture and exposure conditions. It is revealed that competition between the reversible and irreversible optical changes led to unique decay-to-recovery behavior for the QD emission, metastable bright states of QDs that can be activated and deactivated numerous times, and decoupled optical changes (reversible intensity changes vs irreversible spectral shifts). We suggest that the distinct dynamic response of each QD architecture arises from how the core and shell interact with each other and the influence of environment parameters (i.e., oxygen, H2O, and light). Furthermore, there is a large difference in the decay and recovery rates (seconds vs many minutes) to be considered for dynamic photonic systems. This work offers a general framework for evaluating dynamic photoluminescence properties of QDs where stable or variable/controlled emission is required, in situations where long device lifetimes are highly desirable (e.g., QD displays, LEDs, and lasers), or in the case of exploring dynamic properties for tunable emission patterning.

# Stable Molecular Surface Modification of Nanostructured, Mesoporous Metal Oxide Photoanodes by Silane and Click Chemistry\_2019

The exposure of protein pharmaceuticals to light can cause loss of potency, oxidation, structural changes and aggregation. To elucidate the chemical pathways of photodegradation, we irradiated human growth hormone (hGH) at λ = 254 nm, λ ≈ 265–340 nm, and λ ≈ 295–340 nm (using the spectral cutoff of borosilicate glass) and analyzed the products by mass spectrometry. By means of LC-MS/MS analysis, we observed an unusual peptide backbone cleavage between Glu-88 and Pro-89. The crystal structure of hGH indicates that these residues are in proximity to Trp-86, which likely mediates this backbone cleavage. The two cleavage fragments observed by MS/MS analysis indicate the loss of CO from the amide bond and replacement of the Glu–C(═O)Pro bond with a Glu–H bond, accompanied by double bond formation on proline. The reaction is oxygen-independent and likely involves hydrogen transfer to the Cα of Glu-88. To probe the influence of the protein fold, we irradiated hGH in its unfolded state, in 1:1 (v/v) acetonitrile/water, and also the isolated tryptic peptide Ile-78–Arg-90, which contains the Glu-88–Pro-89 sequence. In both cases, the cleavage between Glu-88 and Pro-89 was largely suppressed, while other cleavage pathways became dominant, notably between Gln-84 and Ser-85, as well as Ser-85 and Trp-86.

# Decay-to-Recovery Behavior and on–off Recovery of Photoluminescence Intensity from Core/Shell Quantum Dots\_2017

Solution processed thin film organo-metal halide perovskites are gaining attention as attractive material prospects for low cost visible and near-infrared lasers while benefiting from recent large investments in photovoltaics of this micro/nanocrystalline material class. A number of reports have demonstrated optically pumped laser action in various optical resonator configurations at comparative low thresholds that might ultimately be compatible with corresponding injection currents required for junction lasers. One major question, however, is the inherent material robustness and stability of the perovskites under what are much higher optical and electronic excitation conditions than encountered in photovoltaics, yet typical in the technologically mature epitaxially grown III–V compound semiconductor lasers. Here we assess CH(NH2)2PbBr3 (FAPbBr3) solid thin films embedded within two sputtered planar dielectric HfO2/SiO2 distributed Bragg reflectors (DBRs) in green perovskite vertical-cavity surface-emitting lasers (PeVCSELs). The high quality factor single mode resonator (Q ∼ 1420) enables us to reach lasing threshold at low optical pumping (∼18.3 μJ/cm2) while delivering a temporally and spatially well-defined output beam. The device fabrication approach automatically self-encapsulates the perovskite active layer from the ambient. We report here achieving a device lasing lifetime for up to 20 h (∼108 laser shots) at room temperature under sustained illumination of 355 nm pulsed laser excitations (0.34 ns, 1 kHz). We also show how this PeVCSEL microfabrication route can be generally adapted to many substrates, specifically demonstrating a green perovskite thin film surface-emitting laser on a flexible polymer substrate.

# Photodegradation of Human Growth Hormone: A Novel Backbone Cleavage between Glu-88 and Pro-89\_2013

Lead halide perovskite nanowires (NWs) are emerging as a class of inexpensive semiconductors with broad bandgap tunability for optoelectronics, such as tunable NW lasers. Despite exciting progress, the current organic–inorganic hybrid perovskite NW lasers suffer from limited tunable wavelength range and poor material stability. Herein, we report facile solution growth of single-crystal NWs of inorganic perovskite CsPbX3 (X = Br, Cl) and their alloys [CsPb(Br,Cl)3] and a low-temperature vapor-phase halide exchange method to convert CsPbBr3 NWs into perovskite phase CsPb(Br,I)3 alloys and metastable CsPbI3 with well-preserved perovskite crystal lattice and NW morphology. These single crystalline NWs with smooth end facets and subwavelength dimensions are ideal Fabry–Perot cavities for NW lasers. Optically pumped tunable lasing across the entire visible spectrum (420–710 nm) is demonstrated at room temperature from these NWs with low lasing thresholds and high-quality factors. Such highly efficient lasing similar to what can be achieved with organic–inorganic hybrid perovskites indicates that organic cation is not essential for light emission application from these lead halide perovskite materials. Furthermore, the CsPbBr3 NW lasers show stable lasing emission with no measurable degradation after at least 8 h or 7.2 × 109 laser shots under continuous illumination, which are substantially more robust than their organic–inorganic counterparts. The Cs-based perovskites offer a stable material platform for tunable NW lasers and other nanoscale optoelectronic devices.

# Stable Green Perovskite Vertical-Cavity Surface-Emitting Lasers on Rigid and Flexible Substrates\_2017

The relative position of La and Lb ππ\* electronic states in purine nucleobases is a much debated topic, since it can strongly affect our understanding of their photoexcited dynamics. To assess this point, we calculated the absorption and magnetic circular dichroism (MCD) spectra of adenine, guanine, and their nucleosides in gas-phase and aqueous solution, exploiting recent developments in MCD computational technology within time-dependent density functional theory. MCD spectroscopy allows us to resolve the intense S0→ La transition from the weak S0→ Lb transition. The spectra obtained in water solution, by using B3LYP and CAM-B3LYP functionals and describing solvent effect by cluster models and by the polarizable continuum model (PCM), are in very good agreement with the experimental counterparts, thus providing direct and unambiguous evidence that the energy ordering predicted by TD-DFT, La < Lb, is the correct one.

# Broad Wavelength Tunable Robust Lasing from Single-Crystal Nanowires of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, I)\_2016

Although colloidal quantum dots (QDs) exhibit excellent photostability under mild excitation, intense illumination makes their emission increasingly intermittent, eventually leading to photobleaching. We study fluorescence of two commonly used types of QDs under pulsed excitation with varying power and repetition rate. The photostability of QDs is found to improve dramatically at low repetition rates, allowing for prolonged optical saturation of QDs without apparent photodamage. This observation suggests that QD blinking is facilitated by absorption of light in a transient state with a microsecond decay time. Enhanced photostability of generic quantum dots under intense illumination opens up new prospects for fluorescence microscopy and spectroscopy.

# Relative Stability of the La and Lb Excited States in Adenine and Guanine: Direct Evidence from TD-DFT Calculations of MCD Spectra\_2014

Triplet–triplet-annihilation-based upconversion (TTA-UC) imaging boasts a low-excitation irradiance and an uncanny lack of autofluorescence interference. Because of these promising features, this approach has been the subject of intensifying investigation. Despite the ideal features, the classical approach of TTA-UC imaging suffers from some crucial drawbacks. A major deficiency of the system lies within its poor photostability, especially for a near-IR-excitation system. Here we report a reduction strategy to improve the TTA-UC photostability. The poor photostability of TTA-UC can be attributed to singlet oxygen generation by the sensitizer under irradiation. We control the singlet oxygen by including a reductive solvent, which consumes the singlet oxygen, thereby improving the TTA-UC photostability. We also prepared TTA-UC nanocapsules with reductive solvent soybean oil inside. In comparison to nonreductive solvents such as toluene, our system shows a significant enhancement to the TTA-UC photostability. The prepared TTA-UC nanocapsules were then used for whole-animal deep imaging with a high signal-to-noise ratio.

# Colloidal Quantum Dots as Saturable Fluorophores\_2012

Semiconductor quantum dots (QDs) have attracted extensive attention in various applications because of their unique optical and electronic properties. However, long-term photostability remains a challenge for their practical application. Here, we present a simple method to enhance the photostability of QDs against oxidation by doping aluminum into the shell of core/shell QDs. We demonstrate that Al in the coating shell can be oxidized to Al2O3, which can serve as a self-passivation layer on the surface of the core/shell QDs and effectively stop further photodegradation during long-term light irradiation. The prepared CdSe/CdS:Al QDs survived 24 h without significant degradation when they were subjected to intense illumination under LED light (450 nm, 0.35 W/cm2), whereas conventional CdSe/CdS QDs were bleached within 3 h.

# Highly Photostable Near-IR-Excitation Upconversion Nanocapsules Based on Triplet–Triplet Annihilation for in Vivo Bioimaging Application\_2018

The photostability of fluorescent labels comprises one of the main limitations in single-molecule fluorescence (SMF) and super-resolution imaging. An attractive strategy to increase the photostability of organic fluorophores relies on their coupling to photostabilizers, e.g., triplet excited state quenchers, rendering self-healing dyes. Herein we report the self-healing properties of trisNTA-Alexa647 fluorophores (NTA, N-nitrilotriacetic acid). Primarily designed to specifically label biomolecules containing an oligohistidine tag, we hypothesized that the increased effective concentration of Ni(II) triplet state quenchers would lead to their improved photostability. We evaluated photon output, survival time, and photon count rate of different Alexa647-labeled trisNTA constructs differing in the length and rigidity of the fluorophore-trisNTA linker. Maximum photon output enhancements of 25-fold versus Alexa647-DNA were recorded for a short tetraproline linker, superseding the solution based photostabilization by Ni(II). Steady-state and time-resolved studies illustrate that trisNTA self-healing role is associated with a dynamic excited triplet state quenching by Ni(II). Here improved photophysical/photochemical properties require for a judicious choice of linker length and rigidity, and in turn a balance between rapid dynamic triplet excited state quenching versus dynamic/static singlet excited state quenching. TrisNTA fluorophores offer superior properties for SMF allowing specific labeling and increased photostability, making them ideal candidates for extended single-molecule imaging techniques.

# General Method for the Synthesis of Ultrastable Core/Shell Quantum Dots by Aluminum Doping\_2015

Photosensitizers are reagents that produce reactive oxygen species upon light illumination and are commonly used to study oxidative stress or for photodynamic therapy. There are many available photosensitizers, but most have limitations, such as low photostability, structural instability, or a limited usable range of solvent conditions. Here, we describe a novel photosensitizer scaffold (2I-BDP) based on the unique characteristics of the BODIPY chromophore (i.e., high extinction coefficient, high photostability, and insensitivity to solvent environment). 2I-BDP shows stronger near-infrared singlet oxygen luminescence emission and higher photostability than the well-known photosensitizer, Rose Bengal. Unlike other photosensitizers, this scaffold is widely applicable under various conditions, including lipophilic and aqueous environments. HeLa cells loaded with 2I-BDP could be photosensitized by light illumination, demonstrating that 2I-BDP is potentially useful as a reagent for cell photosensitization, oxidative stress studies, or PDT.

# Tris-N-Nitrilotriacetic Acid Fluorophore as a Self-Healing Dye for Single-Molecule Fluorescence Imaging\_2018

In this paper, we report the first observation of metal-enhanced surface plasmon-coupled phosphorescence (ME-SPCP) from 2,3,7,8,12,17,18-octaethyl-21H,23H-porphyrin platinum II (PtOEP) immobilized in 1% poly(vinyl chloride) (PVC) films on 47 nm continuous gold films coated with 20 and 80 nm silver colloids. In addition to the free space intensity enhancements, increased photostability decay rates, and additional short lifetime components for glass and gold substrates treated with silver colloids, we also observe a pronounced intensity enhancement and photostability of the SPCP signal from the PtOEP/PVC sample on the 47 nm Au films coated with 80 nm Ag colloids. In contrast, we observe a minor enhancement of the SPCP signal from the Au films coated with only 20 nm Ag colloids. The SPCP enhancement from the PtOEP complexes in 1% PVC films on Au films coated with Ag colloids is the first observation of ME-SPCP. In addition, we note the observation of two populations of near-field-induced plasmons:  those facilitating ME-SPCP and noncoupled metal-enhanced free space phosphorescence.

# Highly Efficient and Photostable Photosensitizer Based on BODIPY Chromophore\_2005

Organic dyes usually exhibit enhanced photostability when trapped inside sol−gel silicates. The enhanced photostability is attributed to the reduction of intramolecular motions that facilitate photodegradation. We report the simultaneous detection of mobility and photostability of sol−gel encapsulated didodecyl-3,3,3‘,3‘-tetramethylindocarbocyanine (DiI) using single molecule spectroscopy. Fluorescence from DiI was resolved into parallel and perpendicular polarization components and separately detected. On the basis of the calculated fluorescence polarization, single DiI molecules were classified into “tumbling” and “fixed”. Out of 212 molecules investigated, 52% were found to be fixed. For the first time, the mobility of a guest molecule in sol−gel silicate can be directly correlated with its own photostability. Both tumbling and fixed molecules have shown to exhibit nonuniform photostability, indicative of the very heterogeneous guest−host interactions within each subgroup. The survival lifetimes for the majority of the tumbling and fixed molecules were found to be 4.3 and 13.1 s, respectively, demonstrating unequivocally that fixed molecules exhibit a higher photostability than tumbling molecules. These results are in accordance with a recent study on rhodamine B encapsulated in dried sol−gel silicates.

# Metal-Enhanced Surface Plasmon-Coupled Phosphorescence\_2007

The quest for a solid-state tunable dye laser can be satisfied by sol−gel prepared organic−inorganic hybrids. A photostability study of porous silica−Rhodamine 6G hybrids prepared via a sol−gel method is presented. The dye molecules can be incorporated into the silica matrix by forming weak or covalent bonds (hybrids of classes I and II, respectively). New class II samples and traditional class I materials prepared by the pre-doping method were synthesized. Samples were characterized by photoluminescence measurements to compare the emission properties and the photostability of the samples. The decay of the fluorescence signal as the cumulative excitation energy increases is reported and interpreted by hypothesizing that the dye molecules can be hosted in different surroundings within the porous glass matrix. The reported photoluminescence and photobleaching features indicate the class II samples as good candidates for solid-state dye lasers.

# Probing the Dynamic Guest−Host Interactions in Sol−Gel Films Using Single Molecule Spectroscopy\_2003

We report the synthesis and characterization of a series of boronsubphthalocyanine (BsubPc) dyes which have organic solubility >10–2 M while being amenable to doping into polymeric films. To achieve high solubility we have placed the 3-pentadecylphenoxy molecular fragment in a variety of positions within the BsubPc chemical structure including around the periphery of the BsubPc ligand and in the axial position to the boron atom. We have found that placement of the 3-pentadecylphenoxy molecular fragment around the periphery adversely affects the photostability of the resulting BsubPc whereas placement in the axial position has little effect. We also confirm that the presence of fluorine atoms around the periphery improves the photostability. Overall we present a systematic study of the 3-pentadecylphenoxy fragment as a solubilizing moiety for BsubPc. The nature of the substituents and their position does not affect the nearly pure magenta color characteristic of BsubPc derivatives.

# Hybrid Materials for Solid-State Dye Laser Applications\_2006

A series of crescent-shaped fluorescent dyes (CP1–CP6) were synthesized by hybridizing coumarin and pyronin moieties with different amino substituents at both ends. The molecular structures and photophysical properties of these fluorescent dyes were investigated through X-ray diffraction, absorption spectroscopy, and fluorescence spectroscopy. Results show that the fluorescent dyes exhibited crescent-shaped structures, deep-red emissions (approximately 650 nm), and significant Stokes shifts. In live-cell-imaging experiments, CP1 stains mitochondria, whereas CP3 and CP6 stain the lysosomes in a cytoplasm and the RNA in nucleoli. The relationships between different amino substituent groups and the imaging properties of CP dyes were discussed as well. Additionally, findings from the cytotoxicity and photostability experiments on living cells indicated the favorable biocompatibility and high photostability of the CP dyes.

# Boron Subphthalocyanine Dyes: 3-Pentadecylphenol as a Solubilizing Molecular Fragment\_2011

Fluorescent mitochondrial trackers with the dibenzo[a,f]quinolizinium core are unprecedentedly synthesized by a one-pot protocol starting from commercially available benzaldehydes, anilines, and alkynes through a rhodium(III)-catalyzed cascade C–H N- and C-annulation reaction. Among them, 5g is the most prominent and exhibits high specificity, high efficiency at nanomolar level, superior photostability, and low cytotoxicity.

# Deep-Red Emissive Crescent-Shaped Fluorescent Dyes: Substituent Effect on Live Cell Imaging\_2015

We report on the synthesis and characterization of a PEGylated IR786 GUMBOS (Group of Uniform Materials Based on Organic Salts). The synthesis of this material was accomplished using a three step protocol: (1) substitution of chloride on the cyclohexenyl ring in the heptamethine chain of IR786 by 6-aminohexanoic acid, (2) grafting of methoxy polyethylene glycol (MeOPEG) onto the 6-aminohexanoic acid via an esterification reaction, and (3) anion exchange between [PEG786][I] and lithium bis(trifluoromethylsulfonyl)imide (LiNTf2) or sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in order to obtain PEG786 GUMBOS. Examination of spectroscopic data for this PEG786 GUMBOS indicates a large stokes shift (122 nm). It was observed that this PEG786 GUMBOS associates in aqueous solution to form nano- and mesoscale self-assemblies with sizes ranging from 100 to 220 nm. These nano- and mesoscale GUMBOS are also able to resist nonspecific binding to proteins. PEGylation of the original IR786 leads to reduced cytotoxicity. In addition, it was noted that anions, such as NTf2 and AOT, play a significant role in improving the photostability of PEG786 GUMBOS. Irradiation-induced J-aggregation in [PEG786][NTf2] and to some extent in [PEG786][AOT] produced enhanced photostability. This observation was supported by use of both steady state and time-resolved fluorescence measurements.

# Cascade C–H Annulation Reaction of Benzaldehydes, Anilines, and Alkynes toward Dibenzo[a,f]quinolizinium Salts: Discovery of Photostable Mitochondrial Trackers at the Nanomolar Level\_2018

Derivatives of 2-(2'-hydroxyphenyl) benzotriazole (BZT) are widely used in the coatings industry as effective UV stabilizers. Many commercial stabilizers in this class contain a substituent ortho to the phenolic hydroxyl group. This substitution serves to sterically protect the hydroxyl substituent, which is the structural feature responsible for the photostability of the molecule. A rotamer of BZTs, in which the intramolecular hydrogen-bond has been disrupted, has been implicated in its photodegradation, which occurs in basic, highly polar media. The existence of this form in ortho-unsubstituted BZTs can be detected spectroscopically by differences in both the absorption and emission spectra of the chromophore. Unfortunately, very small spectroscopic differences are seen in differently ortho-substituted BZTs. This contrasts the differences in photostability observed in polar media. As a result, the quantitative use of absorption and fluorescence spectroscopy in the search for more photostable BZTs is precluded. In this work, the superior photostability of a 3'-alpha-cumyl substituted BZT is rationalized in terms of the pronounced conformational preference of this group, first suggested from the results of molecular dynamics (MD) simulations. This result is supported by both solution NMR and solid-state x-ray crystallographic data. In addition, predictions made from the results of further MD runs on the photostability of a differently substituted compound have been experimentally confirmed via loss rate measurements in weathered automotive clearcoats.

# Irradiation Induced Fluorescence Enhancement in PEGylated Cyanine-Based NIR Nano- and Mesoscale GUMBOS\_2012

We have synthesized a new green fluorescent dopant C-545P having incorporated five strategically placed “methyl” steric spacers on the julolidyl ring system. C-545P has good thermal properties and photostability, and when fabricated as a dopant in an Alq3-hosted OLED device, it shows notable improvement in luminance efficiency and is more resistant to concentration quenching than C-545T, particularly in the doping concentration range between 1 and 2% v/v, while achieving comparable device stability.

# Computer Simulations of the Conformational Preference of 3' Substituents in 2-(2'-Hydroxyphenyl) Benzotriazole UV AbsorbersCorrelation with UVA Photopermanence in Coatings\_2001

A new terrylene diimide-based dye (WS-TDI) that is soluble in water has been synthesized, and its photophysical properties are characterized. WS-TDI forms nonfluorescing H-aggregates in water that show absorption bands being blue-shifted with respect to those of the fluorescing monomeric form. The ratio of monomeric WS-TDI to aggregated WS-TDI was determined to be 1 in 14 400 from fluorescence correlation spectroscopy (FCS) measurements, suggesting the presence of a large amount of soluble, nonfluorescent aggregates in water. The presence of a surfactant such as Pluronic P123 or CTAB leads to the disruption of the aggregates due to the formation of monomers in micelles. This is accompanied by a strong increase in fluorescence. A single molecule study of WS-TDI in polymeric films of PVA and PMMA reveals excellent photostability with respect to photobleaching, far above the photostability of other common water-soluble dyes, such as oxazine-1, sulforhodamine-B, and a water-soluble perylenediimide derivative. Furthermore, labeling of a single protein such as avidin is demonstrated by FCS and single molecule photostability measurements. The high tendency of WS-TDI to form nonfluorescent aggregates in water in connection with its high affinity to lipophilic environments is used for the fluorescence labeling of lipid membranes and membrane containing compartments such as artificial liposomes or endosomes in living HeLa cells. The superior fluorescence imaging quality of WS-TDI in such applications is demonstrated in comparison to other well-known membrane staining dyes such as Alexa647 conjugated with dextran and FM 4-64 lipophilic styryl dye.

# Efficient Green Coumarin Dopants for Organic Light-Emitting Devices\_2004

Derivatives and heteroarene analogs of α-T were synthesized and evaluated for their pesticidal activities. Studies on physical properties, photostability, and electronic calculations were also performed on selected analogs. In the nematicide water screen under sun light, some of these compounds were found to be very fast acting and were much more potent than oxamyl and parathion (EC50 = <0.01 ppm at 2 hours). At 1 lb/acre postemergence application 5-chloro-5"-methyloximino-α-T was significantly more active than α-T and completely controlled Johnson grass, yellow foxtail, and morning-glory. However, selected analogs of α-T were found to have poor photostability, with half-life time ranging from 0.7 to 22 hours in thin film photostability studies under solar simulator. Electronic calculations were performed to study the effect of substitution on the ring conformation and the lowest triplet state energy. The calculation results were consistent with the lowest triplet state energy transfer mechanism for singlet oxygen formation.

# A New Photostable Terrylene Diimide Dye for Applications in Single Molecule Studies and Membrane Labeling\_2006

Tracking the dynamics of mitochondrial morphology has attracted much research interest because of its involvement in early stage apoptosis and degenerative conditions. To follow this process, highly specific and photostable fluorescent probes are in demand. Commercially available mitochondria trackers, however, suffer from poor photostability. To overcome this limitation, we have designed and synthesized a fluorescent agent, tetraphenylethene-triphenylphosphonium (TPE-TPP), for mitochondrial imaging. Inherent from the mitochondrial-targeting ability of TPP groups and the aggregation-induced emission (AIE) characteristics of the TPE core, TPE-TPP possesses high specificity to mitochondria, superior photostability, and appreciable tolerance to environmental change, allowing imaging and tracking of the mitochondrial morphological changes in a long period of time.

# 2,2′;5′,2″-Terthiophene and Heteroarene Analogues as Potential Novel Pesticides\_1991

Blended poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1′,3}-thiadiazole)] (PFBT)/poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) conjugated polymer nanoparticles were prepared and characterized by conventional and single-particle fluorescence spectroscopy. The particles exhibit red emission and improved quantum efficiency resulting from highly efficient energy transfer from donor PFBT to acceptor MEH-PPV as well as suppression of MEH-PPV aggregation. Photobleaching results indicate better photostability in the blended sample compared to undoped MEH-PPV nanoparticles and photoactivation of donor emission, which could be useful for single-molecule localization-based super-resolution microscopy. Single blended nanoparticles exhibit bright fluorescence as well as saturation behavior at very low excitation intensities. These and other properties of the blended conjugated polymer nanoparticles could provide substantial improvements in resolution when employed in super-resolution microscopy.

# A Photostable AIE Luminogen for Specific Mitochondrial Imaging and Tracking\_2012

The substituted naphthalene compounds investigated in this paper, i.e., methyl 2-hydroxy-3-naphthoate (MHN23), methyl 1-hydroxy-2-naphthoate (MHN12), and methyl 2-hydroxy-1-naphthoate (MHN21), show a strong intramolecular hydrogen bond (IMHB) in their ground electronic state. The relative position of the IMHB in the naphthalene skeleton acts as a switch and controls the yield of an excited state intramolecular proton transfer (ESIPT) process. As a matter of fact, only MHN23 exhibits a proton transfer (PT) emission and possesses a theoretically proved ESIPT mechanism. The role that the ESIPT mechanism plays on the photostability of the molecule MHN23 is unravelled by comparison with the model compounds methyl salicylate (MS), MHN12, and MHN21. On one hand, the low photoreaction quantum yield, Φr = 0.00015, and therefore the high photostability of MS, under direct ultraviolet (UV) irradiation, has been explained due to the photophysics of its proton transfer tautomer. On the other hand, (a) the two benzene-fused ring derivatives of methyl salicylate, MHN12 and MHN21, also possess a great photostability to UV radiation, and they do not support an ESIPT mechanism; and (b) although MHN23 exhibits an excited state proton transfer, its efficiency is only of 1.8%, and the photostability is 5 times larger than that of MS. As a result, the photostability of MHN23, MHN12, and MHN21 does not rely on the photophysics of their proton transfer tautomers but on the nonradiative dynamics of their respective normal tautomers. We present experimental evidence which supports the above-mentioned statement on the existence of distinctive nonradiative channels for the molecules MHN23, MHN12, and MHN21.

# Photoactivation and Saturated Emission in Blended Conjugated Polymer Nanoparticles\_2013

Several new high μβ chromophores have been synthesized. These chromophores were intentionally designed to study structure−property relationships. The synthetic strategy that was followed has been described in our previous publications. Chromophore photostability was investigated from a structural point of view. Contact and corona poling of the chromophores have also been accomplished with a 70 pm/V r33 being achieved at λ = 1550 nm. The same chromophores were also studied in two different polymer host systems to compare their dependence of the electrooptic coefficient and stability on the matrix material.

# The Six-Membered Intramolecular Hydrogen Bond Position as a Switch for Inducing an Excited State Intramolecular Proton Transfer (ESIPT) in Esters of o-Hydroxynaphthoic Acids\_1999

While research on building-integrated photovoltaics (BIPVs) has mainly focused on power-generating window applications, the utilization of other underutilized surface areas in buildings, including exteriors, facades, and rooftops, has still not been fully explored. The most important requirements for BIPVs are color, power conversion efficiency (PCE), and long-term stability. In this work, we achieved colorful (red, green, blue, RGB) perovskite solar cells (PSCs) with minimized PCE loss (<10%) and enhanced photostability by exploiting the optical properties of nonperiodic multi-nanolayer, narrow-bandwidth reflective filters (NBRFs). The NBRFs were fabricated by multilayering high-index TiO2/low-index SiO2 in a nonperiodic manner, which allowed devices to demonstrate various colors with effectively suppressed unwanted baseline ripple-shape reflectance. The PCEs of PSCs with nonperiodic RGB-NBRFs were 18.0%, 18.6%, and 18.9%, which represent reductions of only 10%, 7%, and 6% of PCE values, respectively, compared to a black control PSC (20.1%). Moreover, the photostability of the PSCs was substantially improved by using the NBRFs because of ultraviolet blocking in the TiO2 layers. The G-PSC retained 65% of the initial PCE after 60 h of continuous illumination (AM 1.5G one sun) at the maximum power point, whereas the black PSC retained only 30%. Aesthetic color value, low PCE loss, and enhanced photostability of PSCs were simultaneously achieved by employing our NBRFs, making this a promising strategy with potential applicability in power-generating building exteriors.

# Synthesis of New Electrooptic Chromophores and Their Structure−Property Relationship\_2004

Chlorophyll a was adsorbed to mesoporous silica (FSM, folded-sheet mesoporous material) to form a chlorophyll−FSM conjugate, in which a nanometer-scale interaction between chlorophyll a molecules resembles a living plant leaf. The mesopores of FSM acted as nanoscale spaces not only for an interaction between chlorophyll molecules and the silica support but also for a nanoscale interaction between the absorbed chlorophyll molecules. These interactions contribute to photostability. An increase in the amount of chlorophyll adsorbed to the pores of FSM leads to an enhancement of the photostability accompanied by a shift in the absorbance maximum to a longer wavelength. The physiological function of the chlorophyll−FSM conjugate was explored as chlorophyll−FSM exhibited the photoinduced ability to catalyze the reduction of methyl viologen (an electron carrier). The evolution of hydrogen gas was observed for 14 h without deterioration when an aqueous suspension containing chlorophyll−FSM, methyl viologen, 2-mercaptoethanol (an electron donor), and platinum was illuminated with visible light.

# Stable and Colorful Perovskite Solar Cells Using a Nonperiodic SiO2/TiO2 Multi-Nanolayer Filter\_2019

We previously reported that constrained 2-phenylbenzo[b]phosphole P-oxides bearing a diphenylamino group show high photostability and thus are promising dyes for fluorescence imaging. Herein we investigated the impact of the bridging moieties on their photophysical properties. A series of benzo[b]phosphole P-oxides constrained with various carbon or silicon bridges were synthesized. All of these compounds showed significant solvatochromism in fluorescence due to the intramolecular charge-transfer character in the excited state. The dipole moments in the excited state for the carbon-bridged derivatives are slightly larger than the silicon-bridged counterparts. Nevertheless, the latter compounds showed orange-red fluorescence in polar solvents with ca. 30 nm red-shifted maxima compared to the carbon analogues. Most importantly, the assessment of their photobleaching resistance revealed that the photostability of this compound series highly relies on the steric bulkiness of the bridging moiety, and even the silicon-bridged derivative can show outstanding photostability, as far as the silicon-bridging moiety has sufficient bulkiness.

# Photostabilized Chlorophyll a in Mesoporous Silica:  Adsorption Properties and Photoreduction Activity of Chlorophyll a\_2002

The photostability of fluorescent dyes is of crucial importance for the statistical accuracy of single-molecule detection (SMD) and for the image quality of scanning confocal microscopy. Concurrent results for the photostability were obtained by two different experimental techniques. First, the photostabilities of several coumarin and rhodamine derivatives in aqueous solution were obtained by monitoring the steady-state fluorescence decay in a quartz cell. Furthermore, an epi-illuminated microscope, continuous wave (CW) excitation at 514.5 nm, and fluorescence correlation spectroscopy (FCS) with a newly developed theory were used to study the photobleaching characteristics of rhodamines under conditions used for SMD. Depending on the rhodamine structure, the probability of photobleaching, pb, is in the order of 10-6−10-7 for irradiances below 103 W/cm2. However, a considerable increase of pb for irradiances above this level was observed which can only be described by photobleaching reactions from higher excited states (two-step photolysis). In view of these observations, the probability of photobleaching, pb, as well as a closed expression of its dependence on the CW excitation irradiance considering a five-level molecular electronic state model with the possibility of photobleaching from higher excited electronic states, is derived. From this model, optimal conditions for SMD with respect to the number of emitted fluorescence photons and to the signal-to-background ratio are discussed, taking into account both saturation and photobleaching. The additional photobleaching due to two-step photolysis limits the applicable irradiance.

# Tuning the Photophysical Properties of Photostable Benzo[b]phosphole P-Oxide-Based Fluorophores\_2017

The insertion of cation impurities into quantum dots (QDs) as a dopant has been proved to be an efficient way to tailor their optical, electronic, and magnetic properties; however, the low quantum yield (QY) and poor photostability strongly limit their further applications. We report a strategy to coat a thin oxide shell around the heterovalent doped QDs to enhance their QYs and photostabilities simultaneously. In the case of Ag+-doped CdS QDs, the controlled cation exchange reaction between Cd2+ and ternary Ag3SbS3 nanoparticles not only realizes the Ag+ doping in CdS QDs but also generates a thin Sb2O3 shell around the surface of the QDs. Enabled by such, as-prepared CdS:Ag@Sb2O3 QDs exhibited enhanced photostability and high QY of 66.5%. We envision that the findings presented here will inspire more novel protocols for advancing the practical applications of doped QDs.

# Photobleaching of Fluorescent Dyes under Conditions Used for Single-Molecule Detection:  Evidence of Two-Step Photolysis\_1998

Metal halide perovskites are attractive candidates for the wide band gap absorber in tandem solar cells. While their band gap can be tuned by partial halide substitution, mixed halide perovskites often have lower open-circuit voltage than would be expected and experience photoinduced trap formation caused by halide segregation. We investigate solar cell performance and photostability across a compositional space of formamidinium (FA) and cesium (Cs) at the A-site at various halide compositions and show that using more Cs at the A-site rather than more Br at the X-site to raise band gap is more ideal as it improves both VOC and photostability. We develop band gap maps and design criteria for the selection of perovskite compositions within the CsxFA1–xPb(BryI1–y)3, space. With this, we identify perovskites with tandem-relevant band gaps of 1.68 and 1.75 eV that demonstrate high device efficiencies of 17.4 and 16.3%, respectively, and significantly improved photostability compared to that of the higher Br-containing compositions.

# High-Performance Quantum Dots with Synergistic Doping and Oxide Shell Protection Synthesized by Cation Exchange Conversion of Ternary-Composition Nanoparticles\_2019

Organometal halide perovskite quantum dots (PQDs) have recently received much attention as a very promising family of materials with excellent performance in electronic and optoelectronic fields, but these perspectives are being restrained by the severe stability, such as chemical and optical degradations. Herein, we propose and demonstrate a facile solution synthesis of nanocomposites of CH3NH3PbX3 (X = Cl, Br, I) PQDs embedded in magnesium silicate hollow spheres. The resultant nanocomposites preserved the strong photoluminescence of the CH3NH3PbX3 PQDs, and the emission peak can be tunable from blue to red region. Photostability tests demonstrated that the nanocomposite samples were obviously more stable than the bare CH3NH3PbX3 PQDs. The photoluminescence (PL) of the nanocomposite sample still remained at 80% after 72 h UV LED illumination, which was much higher than the remnant PL (30%) of the pure CH3NH3PbX3 PQDs. With their high thermal stability and photostability, we demonstrated that these nanocomposites can be used as phosphors in an on-chip UV LED for multicolor display. It offers a facile method to protect perovskite quantum dots and may have great potential applications in solid-state lighting systems with demand of high-color quality such as lasers, displays, and light-emitting diodes.

# Compositional Engineering for Efficient Wide Band Gap Perovskites with Improved Stability to Photoinduced Phase Segregation\_2018

We report the use of europium chelate, 4,4′-bis(1′′,1′′,1′′,2′′,2′′,3′′,3′′-heptafluoro-4′′,6′′-hexanedion-6′′-yl)chlorosulfo-o-terphenyl-Eu3+ (BHHCT-Eu3+), in silver nanostructure-enhanced luminescence and its application to bioassays and bioimaging. The highest luminescence intensity enhancement factor of BHHCT-Eu3+ achieved in this study was about 11 times, while the simultaneously measured luminescence lifetime was reduced 2-fold. The luminophore photostability was also improved by a factor of 3. On the basis of these experimental results, we estimated the impact of silver nanostructures on the excitation and emission enhancement factors. Luminescence enhancement was demonstrated in two geometries: on planar glass substrates and on silica beads. In the biotin-modified IgG antibody assay the bead geometry provided slightly higher enhancement factor and greater sensitivity. Subsequently, we applied such bead substrates to time-gated luminescence imaging of Giardia lamblia cells stained by BHHCT-Eu3+ where we observed improved brightness by a factor of 2. Such improved photostability and brightness of BHHCT-Eu3+ in the presence of metal nanostructures are highly desirable for ultrasensitive bioassays and bioimaging, especially with time gating.

# Nanocomposites of Perovskite Quantum Dots Embedded in Magnesium Silicate Hollow Spheres for Multicolor Display\_2018

Methylammonium lead halide perovskites suffer from poor stability because of their high sensitivity to moisture. Inorganic material coatings of SiO2 are preferred for coupling with perovskites to improve their stability, whereas the conventional SiO2 formation method is unsuitable because it requires water. Here, a simple SiO2 generation method based on the high hydrolysis rate of tetramethyl orthosilicate in analytical-grade toluene was developed to avoid the addition of water and catalyst. As a result, SiO2-encapsulated CH3NH3PbBr3 quantum dots (MAPB-QDs/SiO2) were fabricated without decreasing the quantum yield. Photostability tests indicated that the MAPB-QDs/SiO2 samples were markedly more stable than the unencapsulated MAPB-QDs. The photoluminescence (PL) of the MAPB-QDs/SiO2 powders was maintained at 94.10% after 470 nm LED illumination for 7 h, which was much higher than the remnant PL (38.36%) of the pure MAPB-QD sample under a relative humidity of 60%. Similar test results were observed when the MAPB-QDs/SiO2 powders were incorporated into the poly(methyl methacrylate) films. The enhanced photostability is ascribed to the SiO2 barriers protecting the MAPB-QDs from degradation.

# Europium Chelate (BHHCT-Eu3+) and Its Metal Nanostructure Enhanced Luminescence Applied to Bioassays and Time-Gated Bioimaging\_2010

The photostability of reporter fluorophores in single-molecule fluorescence imaging is of paramount importance, as it dictates the amount of relevant information that may be acquired before photobleaching occurs. Quenchers of triplet excited states are thus required to minimize blinking and sensitization of singlet oxygen. Through a combination of single-molecule studies and ensemble mechanistic studies including laser flash photolysis and time-resolved fluorescence, we demonstrate herein that Ni2+ provides a much desired physical route (chemically inert) to quench the triplet excited state of Cy3, the most ubiquitous green emissive dye utilized in single-molecule studies.

# Enhancing the Stability of CH3NH3PbBr3 Quantum Dots by Embedding in Silica Spheres Derived from Tetramethyl Orthosilicate in “Waterless” Toluene\_2016

The utilization of near-infrared light is an important objective for the high-efficiency utilization of solar energy. Here, we describe a new class of a near-infrared light-induced electron transfer system using a distorted phthalocyanine as a photosensitizer. We revealed that the appropriate modification of distorted phthalocyanine affords a near-infrared absorbing dye with high photostability and long excitation lifetime, and a near-infrared light-induced electron transfer system was successfully established using the dye. The mechanistic investigation clarified that the electron transfer system works via a dynamic quenching mechanism. The system generated a long-lived anion radical species of the dye upon near-infrared light irradiation (>750 nm).

# Cy3 Photoprotection Mediated by Ni2+ for Extended Single-Molecule Imaging: Old Tricks for New Techniques\_2015

A comprehensive study of photodegradation processes in optical sensing materials caused by photosensitized singlet oxygen in different polymers is presented. The stabilities of the polymers are accessed in the oxygen consumption measurements performed with help of optical oxygen sensors. Polystyrene and poly(phenylsilesquioxane) are found to be the most stable among the polymers investigated, whereas poly(2,6-dimethyl-p-phenylene oxide) and particularly poly(methyl methacrylate) and their derivatives show the fastest oxygen consumption. The effect of the stabilizers (singlet oxygen quenchers) on the oxygen consumption rates, the photostability of the sensitizer, and the total photon emission (TPE) by singlet oxygen is studied. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was found to significantly reduce both the TPE and the oxygen consumption rates, indicating its role as a physical quencher of singlet oxygen. The addition of DABCO also significantly improved the photostability of the sensitizer. The N-alkylated derivative of DABCO and DABCO covalently grafted to the polystyrene backbone are prepared in an attempt to overcome the volatility and water solubility of the quencher. These derivatives as well as other tertiary amines investigated were found to be inefficient as stabilizing agents, and some of them even negatively affected the oxygen consumption rates.

# Near-IR Light-Induced Electron Transfer via Dynamic Quenching\_2018

The development of near-infrared fluorescent probes with low pKa, high selectivity, high photostability, and high sensitivity for lysosomal pH detection is of great importance. In the present work, we developed a novel near-infrared lysosomal pH probe (Lyso-hNR) based on a rhodamine derivative. Lyso-hNR showed fast, highly sensitive, and highly selective fluorescence response to acidic pH caused by the H+-induced structure changes from the nonfluorescent spirolactam form to the highly emissive open-ring form. Lyso-hNR displays a significant fluorescence enhancement at 650 nm (over 280-fold) from pH 7.0 to 4.0 with a pKa value of 5.04. Live cell imaging data revealed that Lyso-hNR can selectively monitor lysosomal pH changes with excellent photostability and low cytotoxicity. In addition, Lyso-hNR can be successfully used in tracking lysosomal pH changes induced by chloroquine and those during apoptosis. All these features render Lyso-hNR a promising candidate to investigate lysosome-associated physiological and pathological processes.

# Singlet Oxygen-Induced Photodegradation of the Polymers and Dyes in Optical Sensing Materials and the Effect of Stabilizers on These Processes\_2013

Phototherapy including photodynamic therapy (PDT) and photothermal therapy (PTT) has attracted great attention. However, applications of some photosensitizers remain an obstacle by their poor photostability. To enhance the treatment efficiency of photosensitizers and tumor theranostic effect, herein, we reported a novel carrier-free, theranostic nanodrug by self-assembly of small molecule dual anticancer drugs and photosensitizer for tumor targeting. The developed carrier-free small molecule nanodrug delivery system was formed by hydrophobic ursolic acid, paclitaxel, and amphipathic indocyanine green (ICG) associated with electrostatic, π–π stacking, and hydrophobic interactions exhibiting water stability. The self-assembling of ICG on the dual anticancer nanodrug significantly enhanced water solubility of hydrophobic anticancer drugs and ICG photostability contributing to long-term near-infrared (NIR) fluorescence imaging and effective chemophototherapy of tumor. The in vivo NIR fluorescence imaging showed that the theranostic nanodrug could be targeted to the tumor site via a potential enhanced permeability and retention effect proving the efficient accumulation of nanoparticles in the tumor site. Dramatically, chemophototherapy of tumor-bearing mice in vivo almost completely suppressed tumor growth and no tumor recurrence was observed. Encouraged by its carrier-free, prominent imaging and effective therapy, the small molecule nanodrug via self-assembly will provide a promising strategy for synergistic cancer theranostics.

# Near-Infrared Probe Based on Rhodamine Derivative for Highly Sensitive and Selective Lysosomal pH Tracking\_2017

Fluorescence polarization (FP)-based signal is a self-referencing fluorescence signal, and it is less dependent on dye concentration and environmental interferences, which makes FP measurement an attractive alternative sensing technology to fluorescence intensity-based detection. However, most of the fluorescence polarization probes were constructed by introducing fluorescein, rhodamine, and cyanine dyes, which have relatively shorter excited-state lifetimes compared with BODIPY and naphthalimide dyes. Herein, a first naphthalimide based fluorescence polarization probe (BIO) was designed and synthesized for selective and direct detection of cancer cells. The relatively longer excited-state lifetimes and high photostability of naphthalimide makes BIO more sensitive and accuracy in quantitative determination of HeLa cells in homogeneous solution without cell lysis and further separation steps. The detection limit of BIO for HeLa cells was about 85 cells mL–1, the linear range was from 2.5 × 102 cells mL–1 to 1 × 106 cells mL–1 and the response time is no more than 25 min. Moreover, due to the relatively high photostability of naphthalimide, BIO was particularly suitable for live cell imaging under continuous irradiation with confocal microscopy, and the specific interaction of BIO with CD44-overexpressing cell lines was clearly visualized. Importantly, this BIO based sensing platform offers a direct and real-time tool for cancer cell diagnosis when complemented with the use of naphthalimide-based fluorescence polarization probe.

# A Small Molecule Nanodrug by Self-Assembly of Dual Anticancer Drugs and Photosensitizer for Synergistic near-Infrared Cancer Theranostics\_2017

We describe two reagentless methods of silver deposition for metal-enhanced fluorescence. Silver was deposited on glass positioned between two silver electrodes with a constant current in pure water. Illumination of the glass between the electrodes resulted in localized silver deposition. Alternatively, silver was deposited on an Indium Tin Oxide cathode, with a silver electrode as the anode. Both types of deposited silver produced a 5−18-fold increase in the fluorescence intensity of a nearby fluorophore, indocyanine green (ICG). Additionally, the photostability of ICG was dramatically increased by proximity to the deposited silver. These results suggest the use of silver deposited from pure water for surface-enhanced fluorescence, with potential applications in surface assays and lab-on-a-chip-based technologies, which ideally require highly fluorescent photostable systems.

# Highly Sensitive Naphthalimide-Based Fluorescence Polarization Probe for Detecting Cancer Cells\_2015

We study the impact of excitation energy on the photostability of methylammonium lead triiodide (CH3NH3PbI3 or MAPI) perovskite thin films. Light soaking leads to a transient increase of the photoluminescence efficiency at excitation wavelengths longer than 520 nm, whereas light-induced degradation occurs when exciting the films with wavelengths shorter than 520 nm. X-ray diffraction and extinction measurements reveal the light-induced decomposition of CH3NH3PbI3 to lead iodide (PbI2) for the high-energy excitation regime. We propose a model explaining the energy dependence of the photostability that involves the photoexcitation of residual PbI2 species in the perovskite triggering the decomposition of CH3NH3PbI3.

# Electrochemical and Laser Deposition of Silver for Use in Metal-Enhanced Fluorescence\_2003

In this work, we used monolayer graphene, either underneath or on top of the R6G molecules, to enhance the stability and reproducibility of surface enhanced Raman spectroscopy (SERS). The time evolution of characteristic peaks of the organic molecules was monitored using Raman spectroscopy under continuous light irradiation to quantitatively characterize the photostability. Graphene underneath the organic molecules inhibits the substrate-induced fluctuations; and graphene on top of the organic molecules encapsulates and isolates them from ambient oxygen, greatly enhancing the photostability. Our results showed that the average lifespan of R6G molecules with graphene encapsulation can be increased by about 6-fold under high laser power density (3.67 × 106 W/cm2) and is less dependent on the power density of light irradiation.

# The Role of Excitation Energy in Photobrightening and Photodegradation of Halide Perovskite Thin Films\_2018

Aminobenzofuran-fused rhodamine dyes (AFR dyes) containing an amino group were constructed by an efficient condensation based on 3-coumaranone derivatives. AFR dyes exhibited significantly improved properties, including deep-red and near-infrared emissions, a large Stokes shift, good photostability, and wide pH stability. 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium assay experiments show that these AFR dyes are biocompatible for their low cytotoxicity to both A549 and HeLa cells. Cell imaging data reveal that AFR1, AFR1E, and AFR2 are mainly located in the mitochondria, while AFR3 is a lysosome tracker. As far as we know, NIR AFR3 is the longest fluorescent rhodamine derivative containing the amino group. These amino group-containing AFR dyes hold great potential in fluorogenic detection, biomolecule labeling, and cell imaging.

# Enhanced SERS Stability of R6G Molecules with Monolayer Graphene\_2014

We report a rationale for identifying superior dyes for stimulated-emission depletion (STED) microscopy. We compared the dyes pPDI and pTDI, which displayed excellent photostability in single-molecule spectroscopy. Surprisingly, their photostability and performance in STED microscopy differed significantly. While single pTDI molecules could be visualized with excellent resolution (35 nm), pPDI molecules bleached rapidly under similar conditions. Femtosecond transient absorption measurements proved that the overlap between the stimulated-emission band and the excited-state absorption band is the main reason for the observed difference. Thus, assessment of the excited-state absorption band provides a rational means of dye selection and determination of the optimal wavelength for STED.

# Aminobenzofuran-Fused Rhodamine Dyes with Deep-Red to Near-Infrared Emission for Biological Applications\_2015

In this work, two xanthene dyes (H-hNR and TF-hNR) have been synthesized by a convenient and efficient method. These two dyes exhibited deep-red and near-infrared emissions, high fluorescence quantum yields, and good photostability. Their structure–optical properties were investigated by X-ray crystal structure analysis and density functional theory calculations. Live cell imaging data revealed that H-hNR and TF-hNR could rapidly stain both A549 and HeLa cells with low concentrations. The excellent photophysical and imaging properties render them as promising candidates for use in live cell imaging.

# Spectroscopic Rationale for Efficient Stimulated-Emission Depletion Microscopy Fluorophores\_2010

Metal-enhanced fluorescence (MEF) and delayed fluorescence (alpha α-S1) studies of acriflavin have been undertaken using steady-state and time-resolved fluorescence measurements on silver island films (SiFs) supporting a thin poly(vinyl alcohol) (PVA) polymer film. Nearly a 3.5-fold enhancement in the far-field fluorescence intensity of acriflavin is observed coupled with a decrease in decay times and an improved fluorophore photostability. Our findings are consistent with our proposed model of the coupling and transferring of the excited state energies of fluorophores to silver surface plasmons. Further, an excitation power dependence of MEF is observed in these films, consistent with our postulate of MEF EVE (MEF excitation volumetric effect) and, ultimately, resulting in a ∼7-fold enhancement in fluorescence intensity. Our findings suggest a significant opportunity for the development of shorter-lived, brighter, high photon flux luminescent materials for multifarious applications in the life-sciences.

# Deep-Red and Near-Infrared Xanthene Dyes for Rapid Live Cell Imaging\_2016

High enhancement of fluorescence emission, improved fluorophore photostability, and significant reduction of fluorescence lifetimes have been obtained from high aspect ratio (>100) silver (Ag) nanowires. These quantities are found to depend on the surface loading of Ag nanowires on glass slides, where the enhancement of fluorescence emission increases with the density of nanowires. The surface loading dependence was attributed to the creation of intense electric fields around the network of Ag nanowires and to the coupling of fluorophore excited states that takes place efficiently at a distance of 10 nm from the surface of nanowires, which was confirmed by theoretical calculations. The enhancement of fluorescence emission of fluorescein isothiocyanate (FITC) was assessed by fluorescence spectroscopy and fluorescence-lifetime imaging microscopy (FLIM) to demonstrate the potential of high aspect ratio Ag nanowires. Fluorescence enhancement factors exceeding 14 were observed on Ag nanowires with high loading by FLIM. The photostability of FITC was the highest on nanowires with medium loading under continuous laser excitation for 10 min because of the significant reduction in the fluorescence lifetime of FITC on these surfaces. These results clearly demonstrate the potential of Ag nanowires in metal-enhanced fluorescence-based applications of biosensing on planar surfaces and cellular imaging.

# Metal-Enhanced S1 and Alpha- S1 Fluorescence: Effects of Far-Field Excitation Irradiance on Enhanced Fluorescence\_2014

The near-infrared fluorescent (NIRF) dye, IR780, is recognized as a promising theranostic agent and has been widely investigated for imaging, chemotherapeutic, and phototherapeutic applications. However, its poor photostability and nonselective toxicities toward both cancer and normal cells limit its biological applications. Herein, we introduce the use of GUMBOS (a group of uniform materials based on organic salts) developed through counter-anion exchange with IR780 and subsequent nanomaterials (nanoGUMBOS) formed by complexation with cyclodextrin (CD) for enhanced chemo/photothermal therapy. Such CD-based nanoGUMBOS display improved aqueous stability, photostability, and photothermal effects relative to traditional IR780. The examination of in vitro cytotoxicity reveals that CD-based nanoGUMBOS are selectively toxic toward cancer cells and exhibit synergistically enhanced cytotoxicity toward cancer cells upon NIR laser irradiation. Additionally, in vivo NIRF imaging demonstrated selective accumulation of these nanoGUMBOS within the tumor site, indicating tumor-targeting properties. Further in vivo therapeutic study of these CD-based nanoGUMBOS suggests excellent chemo/photothermal antitumor effects. Using these studies, we herein demonstrate a promising strategy, via conversion of IR780 into nanoGUMBOS, that can be used for improved theranostic cancer treatment.

# Metal-Enhanced Fluorescence from Silver Nanowires with High Aspect Ratio on Glass Slides for Biosensing Applications\_2014

Carbon dots are newly discovered bright fluorescent biolabeling probes that nonspecifically bind to multiple cellular structures. Here we report yellow-orange emissive carbon dots that spontaneously localize inside the nucleolus of HeLa cells, specifically binding to the RNA. Single-particle measurements of carbon dots show fluorescence-intensity fluctuations with superior brightness and photostability. These optical properties were used for performing blinking-assisted localization microscopy that shows organization of the nucleolar RNA with improved resolution. Our study opens up the opportunity for single-molecule imaging and super-resolution microscopy applications using fluorescent carbon dots.

# Tumor-Targeting NIRF NanoGUMBOS with Cyclodextrin-Enhanced Chemo/Photothermal Antitumor Activities\_2019

Novel octupolar fluorophores derived from the symmetrical functionalization of a triphenylamine core with strong acceptor peripheral groups via phenylene-ethynylene linkers have been synthesized and shown to exhibit high fluorescence quantum yields, very large TPA cross-sections in the red−NIR region, and suitable photostability.

# Carbon Dots for Single-Molecule Imaging of the Nucleolus\_2018

Cyanine fluorophores exhibit greatly improved photostability when covalently linked to stabilizers, such as cyclooctatetraene (COT), nitrobenzyl alcohol (NBA), or Trolox. However, the mechanism by which photostabilization is mediated has yet to be determined. Here, we present spectroscopic evidence that COT, when covalently linked to Cy5, substantially reduces the lifetime of the Cy5 triplet state and that the degree of triplet-state quenching correlates with enhancements in photostability observed in single-molecule fluorescence measurements. By contrast, NBA and Trolox did not quench the Cy5 triplet state under our conditions, suggesting that their mechanism of photostabilization is different from that of COT and does not target the fluorophore triplet state directly. These findings provide insights into the mechanisms of fluorophore photostabilization that may lead to improved fluorophore designs for biological imaging applications.

# Enhanced Two-Photon Absorption with Novel Octupolar Propeller-Shaped Fluorophores Derived from Triphenylamine\_2003

Fluorescent silica nanoparticles (FSNPs) are synthesized through the Stöber method by incorporating silane-modified organic dye molecules. The modified fluorescent organic dye molecule is able to be prepared by allylation and hydrosilylation reactions. The optical properties of as-prepared FSNPs are shown the similar optical properties of PR254A (allylated Pigment Red 254) and have outstanding photostability. The polyvinylpyrrolidone (PVP) is introduced onto the surface of FSNP to enhance the binding affinity of PVP-coated FSNP for latent fingerprints (LFPs) detection. The simple preparation and easy control of surface properties of FSNPs show potential as a fluorescent labeling material for enhanced latent fingerprint detection on hydrophilic and hydrophobic substrates in forensic science for individual identification.

# On the Mechanisms of Cyanine Fluorophore Photostabilization\_2012

A 5,6-difluorobenzothiazole-based dibromo monomer was successfully synthesized, from which new fluorinated conjugated polymers PF-ffBTz and PFN-ffBTz were prepared via copolymerizations with two fluorene-based diboronic ester monomers. Twisted fluorene-ffBTz backbones enable PF-ffBTz and PFN-ffBTz with large band gaps up to 3.10 eV and deep-lying highest occupied molecular orbital levels down to −6.2 eV. The chemical structures of PF-ffBTz and PFN-ffBTz impart some new functionalities of fluorinated conjugated polymers. PF-ffBTz can show deep blue electroluminescent emission, with high external quantum efficiency of 3.71%. PFN-ffBTz, with amino-functionalized side chains on the fluorene unit, can serve as an efficient cathode interlayer in inverted polymer solar cells (PSCs), showing better photovoltaic performances if compared with a ZnO interlayer. In addition, it is found that using an optical filter to cut off the short wavelength section (≤380 nm) of incident light can significantly elevate photostability of PSCs under continuous illumination.

# Rapid Imaging of Latent Fingerprints Using Biocompatible Fluorescent Silica Nanoparticles\_2016

Solidification and aqueous redispersion of fluorophores are characteristically challenging because of aggregation quenching and random shifts of emission. Carbon-based polymer dots (PDs) have recently shown photoluminescent (PL) performances superior to those of conventional dyes and inorganic quantum dots (QDs) but suffer from significant fluorescence (FL) quenching and irreversible aqueous dispersion after solidification, which limits their applications in practical biomedicine and optical devices. In this work, we have compared three strategies by utilizing layered double hydroxides (LDHs) to effectively solidify PDs as robust and redispersible composites with well-preserved high brightness against wide pH (pH = 4–12) and strong ionic strength conditions, more stable than the pristine PDs. The resulting PD–LDH nanocomposites also show in vitro/in vivo bioimaging ability with low cytotoxicity and improved photostability. In addition, these composites exhibit high thermal stability at 150 °C for at least 96 h. The composites produced by a one-step physical mixing approach (∼10 min) of LDHs and PDs (p-PLDH) exhibited PL performances comparable to those of the conventional multistep composites (m-PLDH), which require tremendous effort (at least 7 days) to prepare. Structural studies further revealed that the deshaping behavior of PDs and the interflake sandwich assembly of LDHs contributed to the robust FL properties. Because of the simple synthesis, durable photostability, high aqueous redispersion, and multicolor emissions (ranging from blue to near-IR) of these PD–LDH nanocomposites, we believe that they are promising candidates for advanced biorelated technologies and optoelectronics.

# 5,6-Difluorobenzothiazole-Based Conjugated Polymers with Large Band Gaps and Deep Highest Occupied Molecular Orbital Levels\_2018

Nanometer-sized fragments of carbon in the form of multilayer graphene (“carbon dots”) have been under highly active study for applications in imaging. While offering advantages of low toxicity and photostability, such nanomaterials are inhomogeneous and have limited wavelengths of emission. Here we address these issues by assembling luminescent aromatic C16–C38 hydrocarbons together on a DNA scaffold in homogeneous, soluble molecular compounds. Monomer deoxyribosides of five different aromatic hydrocarbons were synthesized and assembled into a library of 1296 different tetramer compounds on PEG-polystyrene beads. These were screened for photostability and a range of emission colors using 365 nm excitation, observing visible light (>400 nm) emission. We identified a set of six oligomers (DNA-carbon assemblies, DNA-CAs) with exceptional photostability that emit from 400 to 680 nm in water, with Stokes shifts of up to 110 nm, quantum yields ranging from 0.01 to 0.29, and fluorescence lifetimes from 3 to 42 ns. In addition, several of these DNA-CAs exhibited white emission in aqueous solution. The molecules were used in multispectral cell imaging experiments and were taken up into cells passively. The results expand the range of emission properties that can be achieved in water with all-hydrocarbon chromophores and establish the use of the DNA scaffold to arrange carbon layers in homogeneous, rapidly synthesized assemblies.

# Achieving Solidification and Redispersion of Semiconducting Polymer Dots by Layered Double Hydroxide Incorporation\_2017

Fluorophores useful for STimulated Emission Depletion (STED) spectroscopy must fulfill strict requirements on depletion efficiency and photostability. These parameters determine the effective resolution of STED imaging. Resolution is typically measured on 30–80 nm spheres heavily decorated with STED bright fluorophores, limiting the possibility to estimate the true resolution achievable on a specific dye. Here we show how single molecule STED microscopy provides an estimate of the fluorophore stimulated emission cross section and of its photostability under STED irradiation. Fluorescein, a green and a yellow mutant of GFP, are tested, and the results are discussed and compared to those obtained with Chromeo488-covered 80 nm spheres on a commercial continuous-wave STED microscope.

# Luminescent Carbon Dot Mimics Assembled on DNA\_2017

The rational design of molecules with selective intracellular targeting is a great challenge for contemporary chemistry and life sciences. Here, we demonstrate a rational approach to development of compartment-specific fluorescent dyes from the γ-aryl substituted pentamethine family. These novel dyes exhibit an extraordinary affinity and selectivity for cardiolipin in inner mitochondrial membrane and possess excellent photostability, fluorescent properties, and low phototoxicity. Selective imaging of live and fixed mitochondria was achieved in various cell lines using nanomolar concentrations of these dyes. Their high localization specificity and low toxicity enables study of morphological changes, structural complexity, and dynamics of mitochondria playing a pivotal role in many pathological diseases. These far-red emitting dyes could also serve in a variety of biomedical applications.

# Stimulated Emission Properties of Fluorophores by CW-STED Single Molecule Spectroscopy\_2013

In a search for environmentally sensitive (solvatochromic) dyes with superior properties, we extended the electronic conjugation of one of the best solvatochromic dyes, Prodan, by substituting its naphthalene core with fluorene. The newly synthesized fluorene derivatives bearing strong electron-donor (dialkylamino) and -acceptor (carbonyl) groups at the 2 and 7 positions showed red-shifted absorption (close to 400 nm), twice as large of a absorption coefficient (43 000 M−1 cm−1), and a manifold larger two-photon absorption cross section (∼400 GM) compared to Prodan. Studies in solvents revealed much stronger fluorescence solvatochromism of the new dyes, which is connected with their twice as large transition dipole moment (14.0 D). Similarly to Prodan, they exhibit high fluorescence quantum yields, while their photostability is largely improved. Thus, substitution of the naphthalene core in Prodan with fluorene resulted in new fluorophores with superior spectroscopic and solvatochromic properties. We expect them to find a variety of applications as environmentally sensitive probes and labels in biology.

# Rational Design of Chemical Ligands for Selective Mitochondrial Targeting\_2013

Through comparing the photocatalytic performance of microscale ZnO, nano ZnO, and Degussa P25 titania (P25), it was found that the microscale ZnO exhibited 2.6−35.7 times higher photocatalytic activity for the photodegradation of various dye pollutants than P25 under both UV−visible and visible irradiation and showed much better photostability than the nano ZnO. The photocatalysts were characterized with XRD, Raman, BET, DRUV−vis, adsorption of dye, photoelectrochemical measurement, and PL. The much higher photocataltyic activity of the microscale ZnO than P25 under UV−visible irradiation is attributed to the higher efficiency of generation, mobility, and separation of photoinduced electrons and holes. The much higher visible photocataltyic activity of the microscale ZnO than P25 is due to the higher photosensitization efficiency of electron transfer from an excited dye to the conduction band of the microscale ZnO than that of P25. The much better photostability of the microscale ZnO than the nano ZnO is due to its better crystallinity and lower defects. The photostability of the microscale ZnO is greatly improved by the surface modification of ZnO with a small amount of TiO2. On the basis of the excellent photocatalytic performance of the microscale ZnO and TiO2-modified ZnO, a novel device of coupling photodegradation with light-to-electricity conversion was developed, which is a promising candidate for the photocatalytic removal of dye pollutants and a renewable energy source.

# Fluorene Analogues of Prodan with Superior Fluorescence Brightness and Solvatochromism\_2010

Highly fluorescent conjugated polymer dots were developed for demanding applications such as fluorescence imaging in live cells. These nanoparticles exhibit small particle diameters, extraordinary fluorescence brightness, and excellent photostability. Single particle fluorescence imaging and kinetic studies indicate much higher emission rates (∼108 s−1) and little or no blinking of the nanoparticles as compared to typical results for single dye molecules and quantum dots. Analysis of single particle photobleaching trajectories reveals excellent photostability—as many as 109 or more photons emitted per nanoparticle prior to irreversible photobleaching. The superior figures of merit of these new fluorescent probes, together with the demonstration of cellular imaging, indicate their enormous potential for demanding fluorescence-based imaging and sensing applications such as high speed super-resolution single molecule/particle tracking and highly sensitive assays.

# Comparison of Dye Photodegradation and its Coupling with Light-to-Electricity Conversion over TiO2 and ZnO\_2009

Boron doped diamond (BDD) thin film was found to exhibit higher photocurrent conversion efficiencies and photostability compared to commonly used transparent conducting oxides (ITO and FTO) owing to the matching energy levels and strong C−C bonding at the organic/diamond interface.

# Multicolor Conjugated Polymer Dots for Biological Fluorescence Imaging\_2008

Xanthophyll carotenoids can self-assemble in aqueous solution to form J- and H-type aggregates. This feature significantly changes the photophysical and optical properties of these carotenoids, and has an impact on solar energy conversion and light induced oxidative damage. In this study we have applied EPR and optical absorption spectroscopy to investigate how complexation can affect the aggregation ability of the xanthophyll carotenoids zeaxanthin, lutein, and astaxanthin, their photostability, and antioxidant activity. It was shown that complexation with the polysaccharide arabinogalactan (AG) polymer matrix and the triterpene glycoside glycyrrhizin (GA) dimer reduced the aggregation rate but did not inhibit aggregation completely. Moreover, these complexants form inclusion complexes with both monomer and H-aggregates of carotenoids. H-aggregates of carotenoids exhibit higher photostability in aqueous solutions as compared with monomers, but much lower antioxidant activity. It was found that complexation increases the photostability of both monomers and the aggregates of xanthophyll carotenoids. Also their ability to trap hydroperoxyl radicals increases in the presence of GA as the GA forms a donutlike dimer in which the hydrophobic polyene chain of the xanthophylls and their H-aggregates lies protected within the donut hole, permitting the hydrophilic ends to be exposed to the surroundings.

# Diamond-Based Molecular Platform for Photoelectrochemistry\_2008

Organic fluorophores for stimulated emission depletion (STED) nanoscopy usually suffer from quenched emission in the aggregate state and inferior photostability, which largely limit their application in real-time, in situ, and long-term imaging at an ultrahigh resolution. Herein, an aggregation-induced emission (AIE) luminogen of DP-TBT with bright emission in solid state (photoluminescence quantum yields = 25%) and excellent photostability was designed to meet the requirements in STED nanoscopy. In addition to its excellent fluorescence properties, DP-TBT could also easily form self-assembling helixes and finally be well-visualized by super-resolution STED nanoscopy. The observations showed that helical fibers of DP-TBT as dashed lines had a much decreased fiber width with also a full width at half-maximum value of only 178 nm, which is ∼6 times higher than solid lines obtained by confocal microscopy (1154 nm). The STED nanoscopic data were also used to reconstruct 3D images of assembled helixes. Finally, by long-term tracking and dynamic monitoring, the formation and growth of helical fibers by DP-TBT in self-assembly processes were successfully obtained. These findings imply that highly emissive AIEgens with good photostability are highly suitable for real-time, in situ, and dynamic imaging at super-resolution using STED nanoscopy.

# Photochemical and Optical Properties of Water-Soluble Xanthophyll Antioxidants: Aggregation vs Complexation\_2013

Efficient organic gain media with high optical gain and good photostability are highly desirable for organic semiconductor lasers. To shed light on the rational molecular design, in this work, a novel deep-blue organic emitter consisting of a carbazole core substituted by a diphenylamine-functionalized triazine unit and two arms of bifluorene with flexible alkyl chains (denoted as C2) was designed and synthesized. Various basic photophysics and amplified spontaneous emission (ASE) characterizations were conducted with a particular focus to unravel the impact of the molecular structure on the photostability. Relatively low ASE threshold of 7.0 μJ/cm2, high net gain coefficient of 79.9 cm–1 (under 40-fold threshold pump fluence), and low optical loss coefficient of 7.0 cm–1 were recorded for C2 in neat films. For comparison, C2 was also dispersed into polystyrene (PS), a low-loss transparent matrix, with various ratios to form PS-C2 blend films. Among them, a 50 wt % PS-C2 blend film exhibited a high gain coefficient of 61.8 cm–1 and a low-loss coefficient of 5.4 cm–1, manifesting enhanced gain properties in comparison with that of pure C2 sample (52.2 and 7.0 cm–1) under identical pump conditions (10-fold threshold pump fluence). With simple high-ratio blending, the photostability and the film morphology stability under annealing conditions were found to be significantly enhanced, giving rise to highly stable optical gain properties. The optical gain properties of the PS-C2 blend films remained almost unchanged even upon harsh annealing treatment in ambient atmosphere. The results suggest an efficient strategy to enhance the photostability of organic gain media without sacrificing the optical gain properties by combining the merits of robust gain media and a low-loss transparent matrix for achieving efficient and stable organic semiconductor lasers.

# Super-Resolution Visualization of Self-Assembling Helical Fibers Using Aggregation-Induced Emission Luminogens in Stimulated Emission Depletion Nanoscopy\_2019

InP/ZnS core/shell nanocrystals are prepared using a single-step heating-up method relying on the difference in reactivity of the applied InP and ZnS precursors. The obtained particles exhibit size-dependent emission in the range of 480−590 nm, a fluorescence quantum yield of 50−70%, and high photostability.

# Enhancing Optical Gain Stability for a Deep-Blue Emitter Enabled by a Low-Loss Transparent Matrix\_2018

Fluorescent dye encapsulated conjugated polymer nanoparticles have been paid significant attention for potential applications in photonics and biophotonics due to their high brightness and better photostability. Bright, photostable, and monodispersed Nile Red (NR) dye encapsulated poly-N-vinylcarbazole (PVK) fluorescent polymer nanoparticles have been prepared to understand the influence of size of particles and the concentration of dye inside the particles on the photophysical properties by using steady-state, time-resolved fluorescence spectroscopy and fluorescence correlation spectroscopy (FCS). Here, we have quantitatively analyzed the hydrodynamic diameter, particle brightness, and population of NR molecules inside the particle with varying the particle size and NR concentration by using fluorescence correlation spectroscopy (FCS). The average fluorescence intensity of a single nanoparticle, i.e., per particle brightness (PPB) value, increases from 80 to 500 kHz, and the number of NR molecules per nanoparticle increases from 5 to 22 by increasing the concentration of NR from 0.5 to 1.8 wt % at the time of nanoparticle preparation. Fluorescence anisotropy study has been undertaken to understand the rotational dynamics of encapsulated NR molecules with varying particle size and NR concentration inside the nanoparticle. The particle brightness and quantum yield are enhanced due to increasing the radiative decay rate. Higher brightness (almost one order of magnitude higher with respect to free dye) and better photostability (15-fold enhancement) of these polymer nanoparticles are found to be efficient for bioimaging purposes.

# One-pot Synthesis of Highly Luminescent InP/ZnS Nanocrystals without Precursor Injection\_2008

Fluorescent biosensors based on environmentally sensitive dyes enable visualization and quantification of endogenous protein activation within living cells. Merocyanine dyes are especially useful for live cell imaging applications, as they are extraordinarily bright, have long wavelengths of excitation and emission, and can exhibit readily detectable fluorescence changes in response to environment. We sought to systematically examine the effects of structural features on key photophysical properties, including dye brightness, environmental responsiveness, and photostability, through the synthesis of a library of 25 merocyanine dyes, derived from combinatorial reaction of 5 donor and 5 acceptor heterocycles. Four of these dyes showed optimal properties for specific imaging applications and were subsequently prepared with reactive side chains and enhanced aqueous solubility using a one-pot synthetic method. The new dyes were then applied within a biosensor design for Cdc42 activation, where dye mero60 showed a remarkable 1470% increase in fluorescence intensity on binding activated Cdc42 in vitro. The dye-based biosensors were used to report activation of endogenous Cdc42 in living cells.

# Photophysics and Dynamics of Dye-Doped Conjugated Polymer Nanoparticles by Time-Resolved and Fluorescence Correlation Spectroscopy\_2013

We synthesized solubilized alkoxysilane-modified perylene derivatives which were covalently attached to an inorganic host matrix, prepared via the sol−gel process. It was shown that the covalent attachment of the alkoxysilane-modified perylenes led to more homogeneous sols and higher concentrations of the dyes in the sol than the physical admixing of corresponding derivatives. Furthermore, we found that modifying the inorganic network with organic groups caused better solubility characteristics for the perylene derivatives. Attachment of the alkoxysilane-modified perylene derivatives was improved using a more reactive network precursor such as zirconium n-propoxide. Monoliths were prepared by using special temperature programs developed for each sol. Photostability tests of these monoliths showed that chemical attachment of the chromophores led to a significant improvement in the photostability in comparison to their physically admixed analogues.

# Environment-Sensing Merocyanine Dyes for Live Cell Imaging Applications\_2013

Spatiotemporal imaging is of enormous use to explore organelle biology, necessitating organelle-tracing techniques reliable in varied cell stress. We herein reported lysosomal imaging using rhodamine-X-integrated sialic acid (ROXSA), which is stably maintained in lysosomes irrespective of lysosomal pH changes. Exhibiting bright fluorescence and superior photostability, ROXSA enables 120 h continual tracking of fusion/fission of lysosomes and mitochondrion–lysosome interaction in mitophagy. Relative to conventional acidotropic probes prone to dissipation from stressed lysosomes, ROXSA offers a new route for long-term tracking of stressed lysosomes relevant to diverse pathological conditions.

# Hybrid Materials Doped with Covalently Bound Perylene Dyes through the Sol−Gel Process\_2000

In this work, we propose a solution-based carbon precursor coating and subsequent carbonization strategy to form a thin protective carbon layer on unstable semiconductor nanostructures as a solution to the commonly occurring photocorrosion problem of many semiconductors. A proof-of-concept is provided by using glucose as the carbon precursor to form a protective carbon coating onto cuprous oxide (Cu2O) nanowire arrays which were synthesized from copper mesh. The carbon-layer-protected Cu2O nanowire arrays exhibited remarkably improved photostability as well as considerably enhanced photocurrent density. The Cu2O nanowire arrays coated with a carbon layer of 20 nm thickness were found to give an optimal water splitting performance, producing a photocurrent density of −3.95 mA cm–2 and an optimal photocathode efficiency of 0.56% under illumination of AM 1.5G (100 mW cm–2). This is the highest value ever reported for a Cu2O-based electrode coated with a metal/co-catalyst-free protective layer. The photostability, measured as the percentage of the photocurrent density at the end of 20 min measurement period relative to that at the beginning of the measurement, improved from 12.6% on the bare, nonprotected Cu2O nanowire arrays to 80.7% on the continuous carbon coating protected ones, more than a 6-fold increase. We believe that the facile strategy presented in this work is a general approach that can address the stability issue of many nonstable photoelectrodes and thus has the potential to make a meaningful contribution in the general field of energy conversion.

# Bifunctional Super-resolution Imaging Probe with Acidity-Independent Lysosome-Retention Mechanism\_2018

Natural amino acids possess side chains with different functional groups (R groups), which make them excellent precursors for programmable synthesis of biomolecule-derived nanodots (biodots) with desired properties. Herein, we report the first systematic study to uncover the material design rules of biodot synthesis from 20 natural α-amino acids via a green hydrothermal approach. The as-synthesized amino acid biodots (AA dots) are comprehensively characterized to establish a structure–property relationship between the amino acid precursors and the corresponding photoluminescent properties of AA dots. It was found that the amino acids with reactive R groups, including amine, hydroxyl, and carboxyl functional groups form unique C–O–C/C–OH and N–H bonds in the AA dots which stabilize the surface defects, giving rise to brightly luminescent AA dots. Furthermore, the AA dots were found to be amorphous and the length of the R group was observed to affect the final morphology (e.g., disclike nanostructure, nanowire, or nanomesh) of the AA dots, which in turn influence their photoluminescent properties. It is noteworthy to highlight that the hydroxyl-containing amino acids, that is, Ser and Thr, form the brightest AA dots with a quantum yield of 30.44% and 23.07%, respectively, and possess high photostability with negligible photobleaching upon continuous UV exposure for 3 h. Intriguingly, by selective mixing of Ser or Thr with another amino acid precursor, the resulting mixed AA dots could inherit unique properties such as improved photostability and significant red shift in their emission wavelength, producing enhanced green and red fluorescent intensity. Moreover, our cellular studies demonstrate that the as-synthesized AA dots display outstanding biocompatibility and excellent intracellular uptake, which are highly desirable for imaging applications. We envision that the material design rules discovered in this study will be broadly applicable for the rational selection of amino acid precursors in the tailored synthesis of biodots.

# Carbon-Layer-Protected Cuprous Oxide Nanowire Arrays for Efficient Water Reduction\_2013

In this study, we report synthesis and characterization of novel carbazole-based group of uniform materials based on organic salts (GUMBOS), as well as potential applications of these compounds. These organic-based compounds exhibit high thermal stability (decomposition temperatures in the range of 395–432 °C) and photostability. In addition, these compounds have appreciably high fluorescence quantum yields (73–99%) with broad emissions in the visible region and quantum yields which depend on the GUMBOS counteranion. The physicochemical, optical, and electrochemical properties of these materials are investigated and detailed here. Evaluation of band gap values (3.4 eV), HOMO–LUMO energy levels, and measured fluorescence quantum yields as compared to carbazole suggest potential use in organic light-emitting diodes. Computational results are found to be complementary to experimental results, and calculated band gaps are in agreement with experimentally obtain values.

# Uncovering the Design Principle of Amino Acid-Derived Photoluminescent Biodots with Tailor-Made Structure–Properties and Applications for Cellular Bioimaging\_2018

The study of π-conjugated oligomers has garnered significant interest because of their use in organic optoelectronic devices, such as organic light-emitting diodes or organic field-effect transistors. Herein, we varied the inner heterocyclic units of pyridyl (Pyr)-capped π-conjugated oligomers consisting of furan (F) and thiophene (T) subunits to afford homomeric (Pyr2F3 and Pyr2T3) and heteromeric (Pyr2F2T and Pyr2T2F) molecules as applicable semiconducting building blocks. The oligomers were synthesized, and their solution- and solid-state spectroscopic properties were characterized. Compared to their thiophene congeners, oligomers with furans directly attached to the pyridyl moieties (Pyr2F3 and Pyr2F2T) gave rise to larger solution-state quantum yields and optical band gaps. Oligomers possessing a central furan subunit (Pyr2F3 and Pyr2T2F), on the other hand, were found to be nearly nonemissive in the solid state, which is attributed to nonradiative decay likely caused by π–π stacking interactions. Unlike the Pyr2T2F hybrid oligomer, Pyr2F2T exhibited not only a comparatively high solution-state quantum yield (7%) but also the brightest solid-state quantum yield emission (5%) and photostability (98%) when evaluated under ambient conditions. Density functional theory (DFT) computations support these trends, indicating that the largest HOMO–LUMO energy gaps and optical band gaps are possessed by Pyr2F3 and Pyr2F2T while those of Pyr2T2F and Pyr2T3 are the lowest among the oligomers considered here (i.e., Pyr2F3 > Pyr2F2T > Pyr2T2F > Pyr2T3). These results suggest that hybrid furan–thiophene oligomers—like that of Pyr2F2T—could serve as viable building blocks for optoelectronic devices, while possessing the positive attributes of both individual heterocycles in a synergistic manner.

# Carbazole-Derived Group of Uniform Materials Based on Organic Salts: Solid State Fluorescent Analogues of Ionic Liquids for Potential Applications in Organic-Based Blue Light-Emitting Diodes\_2014

Owing to its simple operation and minimal generation of pollutants, miniemulsion polymerization has attracted increasing interest in the field of inkjet printing. In this study, different dyes were encapsulated with styrene-co-butyl acrylate copolymers via miniemulsion polymerization. The encapsulated dye/polymer nanoparticles were spherical with an apparent shell–core structure, narrow size distributions, and good thermal stability. These nanoparticles were used as miniemulsion inks that could remain unchanged with good photostability for a long time. The miniemulsion ink was successfully applied to inkjet printing on paper with bright colors and good fluency, and the dyeing of cotton fabrics indicated that these nanoparticles possessed good rubbing and washing fastness. All of these results suggest that the miniemulsion ink is a potential substitute for inks based on traditional dyes in inkjet printing.

# Characterization of Furan- and Thiophene-Containing Bispyridyl Oligomers via Spectroscopic, Electrochemical, and TD-DFT Methods\_2019

Introduction of the dialkylaminophenyl group in position 7 of 3-hydroxychromone changes the orientation of the excited-state dipole moment and leads to superior solvatochromic properties (>170 nm emission shift in aprotic media). The excited-state intramolecular proton-transfer (ESIPT) reaction of 7-aryl-3-hydroxychromones is almost completely inhibited in most solvents. Methylation of the 3-OH abolishes ESIPT completely and also leads to improved photostability. The probes exhibit a ∼100-fold increase in fluorescence intensity and large Stokes shifts upon binding to membranes, reflecting differences in membrane phase and charge by a >40 nm spread in the emission band position.

# Encapsulated Dye/Polymer Nanoparticles Prepared via Miniemulsion Polymerization for Inkjet Printing\_2018

C60 molecules with monomolecular layer state dispersed on the surface of ZnO and formed the hybridized interaction between ZnO and C60. C60-hybridized ZnO photocatalyst showed enhanced photocatalytic activity for the degradation of the organic dye and the photocorrosion of ZnO was successfully inhibited by the hybridization of C60 molecules. The photocorrosion inhibition of ZnO by C60 molecule could be attributed to the reduced activation of surface oxygen atom. The enhanced photocatalytic activity for C60-hybridized ZnO was originated from the high migration efficiency of photoinduced electrons on the interface of C60 and ZnO, which was produced by the interaction of C60 and ZnO with a conjugative π-system. The enhancement degree of photocatalytic activity was strongly depended on the coverage of C60 molecules on the surface of ZnO nanoparticles, and the optimum hybridization effect was found at a weight ratio of 1.5% (C60/ZnO). The hybridization of C60 with semiconductors could be used to improve the photocatalytic activity as well as the photostability.

# Highly Solvatochromic 7-Aryl-3-hydroxychromones\_2012

C60 molecules with monomolecular layer state dispersed on the surface of ZnO and formed the hybridized interaction between ZnO and C60. C60-hybridized ZnO photocatalyst showed enhanced photocatalytic activity for the degradation of the organic dye and the photocorrosion of ZnO was successfully inhibited by the hybridization of C60 molecules. The photocorrosion inhibition of ZnO by C60 molecule could be attributed to the reduced activation of surface oxygen atom. The enhanced photocatalytic activity for C60-hybridized ZnO was originated from the high migration efficiency of photoinduced electrons on the interface of C60 and ZnO, which was produced by the interaction of C60 and ZnO with a conjugative π-system. The enhancement degree of photocatalytic activity was strongly depended on the coverage of C60 molecules on the surface of ZnO nanoparticles, and the optimum hybridization effect was found at a weight ratio of 1.5% (C60/ZnO). The hybridization of C60 with semiconductors could be used to improve the photocatalytic activity as well as the photostability.

# Photocorrosion Inhibition and Enhancement of Photocatalytic Activity for ZnO via Hybridization with C60\_2008

Oligonucleotide-stabilized silver nanoclusters (AgNCs) show promising applications in bioimaging and bio-/chemo-sensing. However, their unsatisfactory photostability limits their practical applications. In this work, fluorescent AgNCs were synthesized in situ in a DNA hydrogel, consisting of cross-linked enzymatically amplified polymeric DNAs with cytosine-rich sequences in the presence of Ag+. The fluorescence property of the resultant AgNCs was optimized by a rational design of the DNA sequences to cover a broad spectrum with comparable green and red emissions. Under the protection of the DNA hydrogel, the AgNCs showed significantly improved photostability in an ambient oxygen environment, as well as low cytotoxicity even at a high concentration. Therefore, these properties show the rolling-circle-amplification-stabilized AgNCs to be a promising possible fluorescent probe for the detection of reactive oxygen/nitrogen species (ROS/RNS) in live cells because red-emitting species are susceptible to oxidation and consequently convert to green-emitting species. Finally, the as-prepared AgNCs were demonstrated to be a sensitive and specific probe for cellular imaging and the monitoring of ROS/RNS levels, which broadens the applications of AgNCs and provides a new tool for related biological investigations.

# Biohydrogen Production from Sucrose Using the Visible Light Sensitization of Artificial Zn Chlorophyll-a\_2002

The prototypical [Ru(bpy)3]2+ (bpy = 2,2′-bipyridine, Ru-1) with 3MLCT state (metal-to-ligand charge-transfer, πM → πL\*) is one of the most widely used photosensitizers (PSs) for photocatalytic hydrogen production. However, its photostability and excited state lifetime (<1 μs) are eagerly to be improved to further enhance the performance of hydrogen production. Herein, [Ru(bpy)2(3-pyrenyl-1,10-phenanthroline)]2+ (Ru-3) with 3IL/3MLCT equilibrated state and [Ru(bpy)2(3-pyrenyl ethynylene-1,10-phenanthroline)]2+(Ru-4) with 3IL state (intraligand charge transfer, πL → πL\*) as lowest excited state were first introduced into the photocatalytic hydrogen evolution system. Photophysical and photocatalytic characteristics manifest that the 3IL state complex (Ru-4) shows a long-lived excited state (up to 120 μs) and much enhanced photostability with no photobleaching over 13 h in stark contrast to Ru-1 and [Ru(bpy)2(1,10-phenanthroline)]2+ (Ru-2). Photocatalytic reactions with these Ru(II) complexes as PSs, Co(dmgH)2pyCl (C-1) as a catalyst, and N, N-dimethyl-p-toluidine (DMT) as an electron donor indicate that the catalytic performance of Ru-4 and Ru-3 is dramatically enhanced compared to that of Ru-2 and Ru-1, and the TON and TOF toward Ru-4 can reach up to 9140 and 6.3 min–1 under the optimized condition. Photoluminescence studies reveal that the Stern–Volmer quenching constant of excited state Ru-4 by DMT is determined as 2.8 × 104 M–1, which is 4.5-, 42-, and 44-fold higher than those of Ru-3 (6.2 × 103 M–1), Ru-2 (6.7 × 102 M–1), and Ru-1 (6.3 × 102 M–1), respectively. Transient absorption spectra confirmed that the reductive quenching mechanism is the dominated process, and the quenching constant of electron transfer from reduced PSs of Ru-1–Ru-4 to C-1 catalyst has the same order of magnitude (∼105 M–1). The increased photocatalytic activity of Ru-3 and Ru-4 is due to their prominent photostability and efficient electron transfer from DMT to PSs. This work not only contributes to a deep understanding in the photocatalytic process with the PSs of three different excited state types but also opens up an avenue to explore robust and long-lived PSs with 3IL state for efficient hydrogen production.

# Highly Stable and Multiemissive Silver Nanoclusters Synthesized in Situ in a DNA Hydrogel and Their Application for Hydroxyl Radical Sensing\_2018

We introduce a fast and simple method, named the potentiostatic electrodeposition technique, to deposit metal particles on the planar surface for application in metal-enhanced fluorescence. The as-prepared metallic surfaces were comprised of silver nanostructures and displayed a relatively homogeneous morphology. Atomic force microscopy and UV−visible absorption spectroscopy were used to characterize the growth process of the silver nanostructures on the indium tin oxide (ITO) surfaces. A typical 20-fold enhancement in the intensity of a nearby fluorophore, [Ru(bpy)3]2+, could be achieved on the silvered surfaces. In addition, the photostability of [Ru(bpy)3]2+ was found to be greatly increased due to the modification of the radiative decay rate of the fluorophore. It is expected that this electrochemical approach to fabricating nanostructured metallic surfaces can be further utilized in enhanced fluorescence-based applications.

# Robust and Long-Lived Excited State Ru(II) Polyimine Photosensitizers Boost Hydrogen Production\_2018

As stimulated emission depletion (STED) microscopy can provide structural details of cells with an optical resolution beyond the diffraction limit, it has become an indispensable tool in cell biology. However, the intense STED laser beam usually causes rapid photobleaching of the employed fluorescent dyes, which significantly limits the utility of STED microscopy from a practical perspective. Herein we report a new design of super-photostable dye, PhoxBright 430 (PB430), comprising a fully ring-fused π-conjugated skeleton with an electron-accepting phosphole P-oxide unit. We previously developed a super-photostable dye C-Naphox by combining the phosphole unit with an electron-donating triphenylamine moiety. In PB430, removal of the amino group alters the transition type from intramolecular charge transfer character to π–π\* transition character, which gives rise to intense fluorescence insensitive to molecular environment in terms of fluorescence colors and intensity, and bright fluorescence even in aqueous media. PB430 also furnishes high solubility in water, and is capable of labeling proteins with maintaining high fluorescence quantum yields. This dye exhibits outstanding resistance to photoirradiation even under the STED conditions and allows continuous acquisition of STED images. Indeed, using a PB430-conjugated antibody, we succeed in attaining a 3-D reconstruction of super-resolution STED images as well as photostability-based multicolor STED imaging of fluorescently labeled cytoskeletal structures.

# Electrochemical Preparation of Silver Nanostructure on the Planar Surface for Application in Metal-Enhanced Fluorescence\_2007

Reversibly switchable fluorescent proteins (RSFPs) can be effectively used for super-resolution optical fluctuation imaging (SOFI) based on the switching and fluctuation of single molecules. Several properties of RSFPs strongly influence the quality of SOFI images. These properties include (i) the averaged fluorescence intensity in the fluctuation state, (ii) the on/off contrast ratio, (iii) the photostability, and (iv) the oligomerization tendency. The first three properties determine the fluctuation range of the imaged pixels and the SOFI signal, which are of essential importance to the spatial resolution, and the last may lead to artificial aggregation of target proteins. The RSFPs that are currently used for SOFI are low in averaged fluorescence intensity in the fluctuation state, photostability, and on/off contrast ratio, thereby limiting the range of application of SOFI in biological super-resolution imaging. In this study, we developed a novel monomeric green RSFP termed Skylan-S, which features very high photostability, contrast ratio, and averaged fluorescence intensity in the fluctuation state. Taking advantage of the excellent optical properties of Skylan-S, a 4-fold improvement in the fluctuation range of the imaged pixels and higher SOFI resolution can be obtained compared with Dronpa. Furthermore, super-resolution imaging of the actin or tubulin structures and clathrin-coated pits (CCPs) in living U2OS cells labeled with Skylan-S was demonstrated using the SOFI technique. Overall, Skylan-S developed with outstanding photochemical properties is promising for long-time SOFI imaging with high spatial-temporal resolution.

# Super-Photostable Phosphole-Based Dye for Multiple-Acquisition Stimulated Emission Depletion Imaging\_2017

The fluorescence signal of single organic fluorophores is characterized by random blinking and irreversible photobleaching. Photoinduced blinking of Cy5 has posed various limitations of this popular near-infrared (NIR) probe in biological applications. Here we show that fluorophore−metal nanoparticle (NP) complexes greatly suppress Cy5 blinking and noticeably reduce photobleaching events. The blinking behavior of single Cy5 molecules was investigated and compared in the absence and the presence of silver nanostructures. A power-law distribution of off time population was observed for single Cy5 molecules. Average off times were compared to evaluate the plasmonic effect of silver nanoparticles on the triplet decay rates. We furthermore demonstrate enhanced photostability in the presence of silver NPs. The results show that plasmonic-controlled fluorescence can lead to a novel physical mechanism to enhance fluorescence intensity, reduce blinking, and increase photostability.

# Development of a Reversibly Switchable Fluorescent Protein for Super-Resolution Optical Fluctuation Imaging (SOFI)\_2015

We developed highly dispersible and photostable nanoparticles of vitamin, folic acid (FA). FA was wet bead milled with milling and dispersing adjuvants and transglycosylated compounds such as α-glucosyl hesperidin (Hesperidin-G) and rutin (Rutin-G), which solubilized FA. The milled slurries of FA particles with transglycosylated compounds consisted of nanosized particles with a median diameter of <100 nm. The lyophilized formulations of these slurries retained their nanometer size after resuspension in water with no aggregation. The apparent solubility of FA in these formulations was 100-fold higher than that of untreated FA. The solubilizing effect of Rutin-G may affect the particle size reduction and dispersibility of FA. The photostability results showed that the strong antioxidant activity of Rutin-G substantially increased the photostability of FA solution. On the basis of these results, bead milling of FA with Rutin-G is a promising technique for developing highly dispersible, photostable nanoparticle FA formulations.

# Reduced Blinking and Long-Lasting Fluorescence of Single Fluorophores Coupling to Silver Nanoparticles\_2008

A new photochromic compound containing a pyrazole-ring unit, 1,3-diphenyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone, was synthesized. Its structure, photochromic properties, and photochemical kinetics were characterized. The results show that the title compound exhibits reversible enol−keto photoisomerization, excellent photostability, and high fatigue resistance. An intra- and intermolecular proton-transfer mechanism is proposed.

# Inhibition of Photodegradation of Highly Dispersed Folic Acid Nanoparticles by the Antioxidant Effect of Transglycosylated Rutin\_2016

Photostability, inherent fluorescence brightness, and optical modulation of fluorescence are key attributes distinguishing silver nanoclusters as fluorophores. DNA plays a central role both by protecting the clusters in aqueous environments and by directing their formation. Herein, we characterize a new near-infrared-emitting cluster with excitation and emission maxima at 750 and 810 nm, respectively, that is stabilized within C3AC3AC3TC3A. Following chromatographic resolution of the near-infrared species, a stoichiometry of 10 Ag/oligonucleotide was determined. Combined with excellent photostability, the cluster’s 30% fluorescence quantum yield and 180 000 M−1 cm−1 extinction coefficient give it a fluorescence brightness that significantly improves on that of the organic dye Cy7. Fluorescence correlation analysis shows an optically accessible dark state that can be directly depopulated with longer wavelength coillumination. The coupled increase in total fluorescence demonstrates that enhanced sensitivity can be realized through Synchronously Amplified Fluorescence Image Recovery (SAFIRe), which further differentiates this new fluorophore.

# Synthesis and Solid-State Photochromism of 1,3-Diphenyl-4- (2-chlorobenzal)-5-hydroxypyrazole 4-Methylthiosemicarbazone\_2007

Pyrene is a good oxygen-sensitive probe with high fluorescence quantum yield, suitable sensitivity, and high photostability when dispersed in gas-permeable organic polymers, but it is a carcinogen and environmental pollutant and tends to aggregate and/or evaporate at high temperature/low pressure. In this work, we show that pyrene can be easily and firmly encapsulated in a metal–organic zeolite SOD-[Zn(mim)2] (Hmim = 2-methylimidazole, MAF-4 or ZIF-8) via an in situ loading strategy, giving fluorescence O2-sensing materials not only with fast response, high photostability, and tunable sensitivity but also free of pyrene aggregation/leak and interference by other quenchers. Moreover, these host–guest inclusion crystals can be easily fabricated as thin film sensors and aerodynamic coatings.

# DNA Encapsulation of 10 Silver Atoms Producing a Bright, Modulatable, Near-Infrared-Emitting Cluster\_2010

Rational design and preparation of bioinspired polydopamine (PDA)-based synthetic melanin hybrid materials with well-controlled morphologies and improved properties face a grand challenge at the current situation. Herein, we report the facile fabrication of photocatalytic CdS@PDA patchy nanoparticles with tunable inorganic patchy densities via different Cd2+-loaded PDA precursors. Both of “postdoping” and “predoping” strategies can be used to fabricate CdS@PDA hybrid NPs with distinct CdS patchy densities, which could further induce distinct physical properties and catalytic behaviors. Those resulting functional nanocomposites exhibited significantly enhanced photoactivity and photostability toward the catalytic degradation of methylene blue under visible light irradiation. We believe that the excellent adsorption, redox potential, and free-radical scavenging properties of PDA substrates could provide the outstanding photoactivity and photostability for CdS photocatalytic reaction. This work could inspire more kinds of synthetic melanin-based functional hybrids for stable, efficient, and sustainable photocatalysis.

# Encapsulating Pyrene in a Metal–Organic Zeolite for Optical Sensing of Molecular Oxygen\_2015

We present a perfluorocarbon-hydrocarbon amphiphilic cyanine dye that J-aggregates in fluorous solvent. J-Aggregation is a special type of fluorophore aggregation, affording enhanced photophysical properties. Cyanine dyes are excellent J-aggregators in water but, until now, cyanine J-aggregates have not been translated to nonaqueous media. The fluorous phase J-aggregate displays enhanced photostability and processability compared to analogous aqueous aggregates.

# Synthetic Melanin Hybrid Patchy Nanoparticle Photocatalysts\_2019

The development of straightforward accesses to organic functional materials through C–H activation is a revolutionary trend in organic synthesis. In this article, we propose a concise strategy to construct a large library of donor–acceptor-type biheteroaryl fluorophores via the palladium-catalyzed oxidative C–H/C–H cross-coupling of electron-deficient 2H-indazoles with electron-rich heteroarenes. The directly coupled biheteroaryl fluorophores, named Indazo-Fluors, exhibit continuously tunable full-color emissions with quantum yields up to 93% and large Stokes shifts up to 8705 cm–1 in CH2Cl2. By further fine-tuning of the substituent on the core skeleton, Indazo-Fluor 3l (FW = 274; λem = 725 nm) is obtained as the lowest molecular weight near-infrared (NIR) fluorophore with emission wavelength over 720 nm in the solid state. The NIR dye 5h specifically lights up mitochondria in living cells with bright red luminescence. Typically, commercially available mitochondria trackers suffer from poor photostability. Indazo-Fluor 5h exhibits superior photostability and very low cytotoxicity, which would be a prominent reagent for in vivo mitochondria imaging.

# Fluorescent Cyanine Dye J-Aggregates in the Fluorous Phase\_2018

The application of aggregation-induced emission luminogens (AIEgens) has heralded a new age in the analysis of subcellular events and has overcome many of the limitations of conventional fluorescent probes. Despite the extensive literature investigating AIEgens in mammalian cells, few reports exist of their bioimaging applications in plant cells. In this report, we describe the first systematic investigation of the uptake, distribution, and bioimaging applications of AIEgens and AIE saponin nanoparticles in the plant model system Arabidopsis thaliana. We find that the superior photostability, high colocalization with fluorescent proteins, and unique tissue-specific turn-on emission properties make AIEgens well-suited to tackle the emergent challenges faced in plant bioimaging.

# Unparalleled Ease of Access to a Library of Biheteroaryl Fluorophores via Oxidative Cross-Coupling Reactions: Discovery of Photostable NIR Probe for Mitochondria\_2016

Several novel fluorinated fluoresceins (Oregon Green dyes) were prepared by the reaction of fluororesorcinols with phthalic anhydride and its derivatives. A novel regiospecific synthesis of fluororesorcinols was key to the successful synthesis of these new fluorophores. (Polyfluoro)nitrobenzenes were reacted with 2 equiv of sodium methoxide followed by reduction, hydrodediazoniation, and demethylation, giving the first straightforward synthesis of 2-fluororesorcinol, 4-fluororesorcinol, 2,4-difluororesorcinol, and 2,4,5-trifluororesorcinol. These fluorinated fluoresceins have higher photostability and ionize at a lower pH (pKa = 3.3−6.1) than fluorescein (pKa = 6.5). Some of the fluorinated fluoresceins have very high quantum yields (0.85−0.97), which, in combination with their lower pKas and high photostability, makes them superior fluorescent dyes for use as reporter molecules in biological systems.

# Uptake, Distribution, and Bioimaging Applications of Aggregation-Induced Emission Saponin Nanoparticles in Arabidopsis thaliana\_2017

Soluble and stable zethrenebis(dicarboximide) (1) was synthesized by an in situ Stille cross coupling/transannular cyclization reaction. 1 showed largely improved photostability and solubility compared with the very unstable zethrene and it also exhibited far-red absorption and emission with high photoluminescence quantum yield. Bromination of 1 with NBS/DMF gave its quinone form 2 via an unusual pathway.

# Synthesis of Fluorinated Fluoresceins\_1997

A phalloidin-functionalized hyperbranched conjugated polyelectrolyte (HCPE-phalloidin) is synthesized and used for direct filamentous actin (F-actin) imaging in living Hela cells. Different from commercially available organic dye-phalloidin conjugates, which require sophisticated techniques to be delivered into living cells, simple incubation of living cells with HCPE-phalloidin leads to efficient internalization of the probe and clear visualization of F-actin due to high brightness of HCPE and good specificity between phalloidin and actin. In addition, HCPE-phalloidin possesses improved photostability as compared to that for commercially available Alexa Fluor 488-phalloidin conjugates, suggesting that the new probe is promising for long-term F-actin imaging in living cells. Further fine-tuning the fluorescent property and targeting ability of HCPE-based probes could lead to more complicated imaging applications and subcellular target detection.

# Soluble and Stable Zethrenebis(dicarboximide) and Its Quinone\_2010

Successful integration of selenium unit into a newly designed cationic chemical architecture led to the development of a highly photostable molecular maker PA5 to be used in fluorescence microscopy as cellular nucleus staining agent for longer duration imaging under continuous laser illumination. Adaptation of a targeted single-atom modification strategy led to the development of a series of proficient DNA light-up probes (PA1–PA5). Further, their comparative photophysical studies in the presence of DNA revealed the potential of electron rich heteroatoms of chalcogen family in improving binding efficiency and specificity of molecular probes toward DNA. The findings of cell studies confirmed the outstanding cell compatibility of probe PA5 in terms of cell permeability, biostability, and extremely low cytotoxicity. Moreover, the photostability experiment employing continuous laser illumination in solution phase as well as in cell assay (both fixed and live cells) revealed the admirable photobleaching resistance of PA5. Finally, while investigating the phototoxicity of PA5, the probe was found not to exhibit light-induced toxicity even when irradiated for longer duration. All these experimental results demonstrated the promising standing of PA5 as a futuristic cell compatible potential stain for bioimaging and temporal profiling of DNA.

# Phalloidin-Functionalized Hyperbranched Conjugated Polyelectrolyte for Filamentous Actin Imaging in Living Hela Cells\_2011

Visualizing and dynamic tracking lipid droplets (LDs) are of great importance to biological research. Herein, two-photon absorption fluorescent small bioprobes based on lipophilic coumarin were developed, which exhibited high selectivity toward LDs in HeLa cells. Because of good biocompatibility and excellent photostability, the probes were applied to realize specific super-resolution visualization of the intracellular LDs in HeLa cells, offering us the quantitative results of the amount and diameters of LDs as well. Furthermore, the bioprobes were capable of monitoring the movements of the LDs in real time. We believe that bioprobes would provide new avenues to designing bioimaging and biological diagnosis.

# Selenium Incorporated Cationic Organochalcogen: Live Cell Compatible and Highly Photostable Molecular Stain for Imaging and Localization of Intracellular DNA\_2016

6,13-Dibromopentacene [2,3:9,10]-bis(dicarboximide) (1) was synthesized for the first time by using in situ generated benzo[1,2-c:4,5-c′]difuran as a key intermediate. Compound 1 exhibits good photostability in comparison to other pentacene derivatives and it can be further functionalized by Pd-catalyzed coupling reactions to give a series of soluble and stable functional pentacenes.

# Coumarin-Based Fluorescent Probes for Super-resolution and Dynamic Tracking of Lipid Droplets\_2018

We have achieved high-efficiency polycrystalline perovskite light-emitting diodes (PeLEDs) based on formamidinium (FA) and cesium (Cs) mixed cations without quantum dot synthesis. Uniform single-phase FA1–xCsxPbBr3 polycrystalline films were fabricated by one-step formation with various FA:Cs molar proportions; then the influences of chemical composition on film morphology, crystal structure, photoluminescence (PL), and electroluminescence (EL) were systematically investigated. Incorporation of Cs+ cations in FAPbBr3 significantly reduced the average grain size (to 199 nm for FA:Cs = 90:10) and trap density; these changes consequently increased PL quantum efficiency (PLQE) and PL lifetime of FA1–xCsxPbBr3 films and current efficiency (CE) of PeLEDs. Further increase in Cs molar proportion from 10 mol % decreased crystallinity and purity, increased trap density, and correspondingly decreased PLQE, PL lifetime, and CE. Incorporation of Cs also increased photostability of FA1–xCsxPbBr3 films, possibly due to suppressed formation of light-induced metastable states. FA1–xCsxPbBr3 PeLEDs show the maximum CE = 14.5 cd A–1 at FA:Cs = 90:10 with very narrow EL spectral width (21–24 nm); this is the highest CE among FA-Cs-based PeLEDs reported to date. This work provides an understanding of the influences of Cs incorporation on the chemical, structural, and luminescent properties of FAPbBr3 polycrystalline films and a breakthrough to increase the efficiency of FA1–xCsxPbBr3 PeLEDs.

# 6,13-Dibromopentacene [2,3:9,10]-Bis(dicarboximide): A Versatile Building Block for Stable Pentacene Derivatives\_2011

Advances in the development of fluorescent carbon dots (CDs) for detecting nitro-explosives have attracted great interest. However, developing long-wavelength luminescence CDs for highly selective determination of 2,4,6-trinitrophenol (TNP) and getting insight into the detection mechanism remain further to be investigated. Here, excitation-independent yellow-green emission CDs with good photostability and low biotoxicity were introduced for detecting TNP selectively. Then, two types of electron transfer (ET) processes including hydrogen-bond interaction-assisted ET and proton transfer-assisted ET are suggested to be responsible for their photophysical behavior. Finally, the visual detection of TNP has been successfully developed by a CD-based indicator paper. The facile, highly sensitive, and selective detection for TNP in both of a solution and a solid phase makes CDs potentially useful in environmental sensor applications.

# High-Efficiency Polycrystalline Perovskite Light-Emitting Diodes Based on Mixed Cations\_2018

Thioether-containing poly(para-phenylene-ethynylene) (PPE) copolymers show a strong fluorescence turn-on response when exposed to oxidants in solution as a result of the selective conversion of thioether substituents into sulfoxides and sulfones. We propose that the increase in fluorescence quantum yield (ΦF) upon oxidation is the result of both an increase in the rate of fluorescence (kF), as a result of greater spatial overlap of the frontier molecular orbitals in the oxidized materials, and an increase in the fluorescence lifetime (τF), due to a decrease in the rate of nonradiative decay. Contrary to established literature, the reported sulfoxides do not always act as fluorescence quenchers. The oxidation is accompanied by spectral changes in the absorption and emission of the polymers, which are dramatic when oxidation causes the copolymer to acquire a donor−acceptor interaction. The oxidized polymers have high fluorescence quantum yields in the solid state, with some having increased photostability. A turn-on fluorescence response to hydrogen peroxide in organic solvents in the presence of an oxidation catalyst indicates the potential of thioether-containing materials for oxidant sensing. The reported polymers show promise as new materials in applications where photostability is important, where tunability of emission across the visible spectrum is desired, and where efficient emission is an advantage.

# Photostable and Low-Toxic Yellow-Green Carbon Dots for Highly Selective Detection of Explosive 2,4,6-Trinitrophenol Based on the Dual Electron Transfer Mechanism\_2018

A series of platinum(II) acetylide complexes containing p-phenylenevinylene and moieties end-capped with triphenylamine groups have been incorporated into poly(methyl methacrylate) (PMMA) monoliths for optical power limiting applications. The one- and two-photon photophysical properties were investigated and compared to the photophysical properties in THF. The absolute two-photon absorption cross-section values for the monolith samples were measured and are comparable to the values obtained in solution. In the PMMA monoliths, the complexes retained the important two-photon absorption and reverse saturable absorption properties necessary for optical power limiting via dual mode mechanism, and their strong nonlinear absorption property was demonstrated by the open-aperture Z-scan method. Photostability studies of the p-phenylenevinylene platinum(II) acetylide complexes showed two photodegradation processes: a trans-to-cis isomerization and a singlet-oxygen sensitized self-oxidative cleavage. The photostability of the least photostable complex TPV0 was increased upon incorporation into a PMMA matrix.

# Conjugated Polymers That Respond to Oxidation with Increased Emission\_2010

The synthesis, structural characterization, and lasing properties of new dye-sensitized organic scattering gain medium based on Rhodamine 6G (Rh6G) confined in polymeric nanoparticles are reported. We have demonstrated coherent laser action from amplifying random media using dye confined into polymeric nanoparticles as scattering centers and gain media. Lasing efficiency and photostability were significantly enhanced by nonresonant feedback of the emission by multiple scattering.

# Polymer Monoliths Containing Two-Photon Absorbing Phenylenevinylene Platinum(II) Acetylide Chromophores for Optical Power Limiting\_2015

We examined the effects of metallic silver colloids on the fluorescence spectral properties of indocyanine green (ICG), which is a dye widely used for in vivo medical testing. Silver colloids from a suspension bind spontaneously to amine-coated surfaces. These colloid-coated surfaces were found to cause a 30-fold increase in the intensity of ICG, which was held close to the metal surface by adsorbed albumin. The increased intensities of ICG were also associated with decreased lifetimes and increased photostability, which are indicative of modifying the fluorophores radiative decay rate. These results suggest the use of metal colloid-enhanced ICG for applications to retinal angiography and vascular imaging and as a contrast agent for optical tomography.

# Conventional Unidirectional Laser Action Enhanced by Dye Confined in Nanoparticle Scatters\_2010

Particulate aluminum films of varied thicknesses were deposited on quartz substrates by thermal evaporation. These nanostructured substrates were characterized by scanning electron microscopy (SEM). With the increase of aluminum thickness, the films progress from particulate toward smooth surfaces as observed by SEM images. To date, metal-enhanced fluorescence (MEF) has primarily been observed in the visible−NIR wavelength region using silver or gold island films or roughened surfaces. We now show that fluorescence could also be enhanced in the ultraviolet-blue region of the spectrum using nanostructured aluminum films. Two probes, one in the ultraviolet and another one in the blue spectral region, have been chosen for the present study. We observed increased emission, decrease in fluorescence lifetime, and increase in photostability of a DNA base analogue 2-aminopurine and a coumarin derivative (7-HC) in 10-nm spin-casted poly(vinyl alcohol) film on Al nanostructured surfaces. The fluorescence enhancement factor depends on the thickness of the Al films as the size of the nanostructures formed varies with Al thickness. Both probes showed increased photostability near aluminum nanostructured substrates, which is consistent with the shorter lifetime. Our preliminary studies indicate that Al nanostructured substrates can potentially find widespread use in MEF applications particularly in the UV-blue spectral regime. Furthermore, these Al nanostructured substrates are very stable in buffers that contain chloride salts compared to usual silver colloid-based substrates for MEF, thus furthering the usefulness of these Al-based substrates in many biological assays where high concentration of salts are required. Finite-Difference Time-Domain calculations were also employed to study the enhanced near-fields induced around aluminum nanoparticles by a radiating fluorophore, and the effect of such enhanced fields on the fluorescence enhancement observed was discussed.

# Metal-Enhanced Fluorescence (MEF) Due to Silver Colloids on a Planar Surface:  Potential Applications of Indocyanine Green to in Vivo Imaging\_2003

Multiwalled carbon nanotubes (MWCNTs)/CdS nanocomposites containing different MWCNT contents were synthesized hydrothermally via direct growth of CdS nanoparticles on the functionalized MWCNT surface. The effects of the hydrothermal temperature and MWCNT content in the nanocomposites on the photoactivity for hydrogen production were investigated comparatively under visible light (λ ≥ 420 nm) irradiation. It was found that 10 wt % MWCNTs/CdS showed much higher photocatalytic hydrogen production efficiency and photostability than the pure CdS nanoparticles. The significantly enhanced photoactivity of the nanocomposite was attributed to the synergetic effect of the intrinsic properties of its components, such as excellent charge transfer and separation on the interfaces between the modified MWCNTs and CdS nanoparticles, resulting from the direct growth of CdS nanoparticles on the MWCNT surface during the hydrothermal process. The present MWCNTs/CdS nanocomposite reveals obvious predominance, such as enhanced visible-light-driven photoactivity and photostability of CdS for hydrogen production.

# Aluminum Nanostructured Films as Substrates for Enhanced Fluorescence in the Ultraviolet-Blue Spectral Region\_2007

High quality CdS/ZnS:Cu quantum dots (QDs) were first synthesized via a green microwave irradiation route. As-prepared core/shell doped QDs presented a strong absorption in the blue light region and highly efficient red to deep red emission with a maximum quantum yield of 40%. The composite formed by dispersing CdS/ZnS:Cu QDs into silicone resin showed an excellent photostability under blue illumination. Finally, high color rendition white light was generated from the CdS/ZnS:Cu QDs-assisted phosphor-converted white light-emitting diode (WLED) in which there was no reabsorption between quantum dots and phosphors. Under operation of 40 mA forward bias current, the fabricated WLED emitted bright natural white light with a high color rendering index of 90, a luminous efficiency of 46.5 lm/W, and the correlated color temperature of 6591 K. Simultaneously, the good color stability was accompanied by the CIE color coordinates of (0.3155, 0.3041) under different forward bias currents.

# Hydrothermal Preparation of Multiwalled Carbon Nanotubes (MWCNTs)/CdS Nanocomposite and Its Efficient Photocatalytic Hydrogen Production under Visible Light Irradiation\_2011

Extension of the π-system of 1,6,7,12-tetrakis(aryloxy)-3,4,9,10-perylenetetracarboxdiimide was achieved by the condensation of 1,6,7,12-tetrakis(aryloxy)-3,4,9,10-perylenetetracarboxylic bisanhydride with 1,2-diaminobenzene, 1,8-diaminonaphthalene, and 9,10-diaminophenanthrene. A full characterization of the resulting novel long-wavelength absorbing dyes by field-desorption mass spectrometry, UV−vis, IR, and 1H and 13C NMR spectroscopies is given. Photostability and thermal stability are reported and discussed.

# Microwave-Assisted Synthesis of CdS/ZnS:Cu Quantum Dots for White Light-Emitting Diodes with High Color Rendition\_2015

Fluorescent core−shell CdTe@SiO2 particles with controllable particle sizes were prepared via a reverse microemulsion method by hydrolyzing tetraethyl orthosilicate within microwater droplets. Aqueous CdTe nanocrystals and CdS nanocrystals stabilized by different types of thiol molecules were prepared for elucidating the mechanism leading to the core−shell structures. Photo-oxidation experiments were performed to show the enhancement effect of the silica shell on the photostability of the CdTe nanocrystals encapsulated. Further surface modifications were also performed for grafting amino groups on the surface of the resultant fluorescent CdTe@SiO2 particles.

# Synthesis of Soluble Perylenebisamidine Derivatives. Novel Long-Wavelength Absorbing and Fluorescent Dyes\_1997

We report a novel kind of oxidized silicon nanospheres (O-SiNSs), which simultaneously possess excellent aqueous dispersibility, high photoluminescent quantum yield (PLQY), ultra photostability, wide pH stability, and favorable biocompatibility. Significantly, the PLQY of the O-SiNSs is as high as 25%, and is stable under intense UV irradiation and in acidic-to-basic environments covering the pH range 2−12. To our best knowledge, it is the first example of water-dispersed silicon nanoparticles which possess both high PLQY and robust pH stability suitable for broad utility in bioapplications. Furthermore, the O-SiNSs are readily conjugated with antibody, and the resultant O-SiNSs/antibody bioconjugates are successfully applied in immunofluorescent cell imaging. The results show that the highly luminescent and stable O-SiNSs/antibody bioconjugates are promising fluorescent probes for wide-ranging bioapplications, such as long-term and real-time cellular labeling.

# Coating Aqueous Quantum Dots with Silica via Reverse Microemulsion Method:  Toward Size-Controllable and Robust Fluorescent Nanoparticles\_2007

Fluorescent micro- and nanosized particles have a broad range of applications in biology, medicine, and engineering. For these uses, the materials should have high emission efficiency and good photostability. However, many organic fluorophores suffer from aggregation-induced quenching effects and photobleaching. Here, we used a simple method based on covalently blending a fluorescent conjugated oligomer with silica nanoparticles to achieve emission quantum yields as high as 97%. The resulting system also showed excellent stability under continuous light illumination, in a range of pH values and temperatures, and in common solvents. This fluorescent material showed outstanding properties, including highly efficient blue emission, low cost, low toxicity, and easy synthesis. Furthermore, its effectiveness for latent fingerprint detection was demonstrated as a proof of concept on various substrates. The obtained emissive fingerprint powder gave good optical/fluorescent images with high contrast and resolution between the ridges and spaces.

# Photo and pH Stable, Highly-Luminescent Silicon Nanospheres and Their Bioconjugates for Immunofluorescent Cell Imaging\_2009

Core–shell (CS) quantum dots (QDs) are promising light absorbers for solar cell applications mainly because of their enhanced photostability compared with bare QDs. Moreover, the superb photostability can be combined with a low number of defects by using CSQDs with a gradient composition change from the core to the shell. Here, we study electron injection from the gradient CSQDs to ZnO nanoparticles. We observe the typical exponential injection rate dependence on the shell thickness (β = 0.51 Å–1) and discuss it in light of previously published results on step-like CSQDs. Despite the rapid drop in injection rates with shell thickness, we find that there exists an optimum thickness of the shell layer at ∼1 nm, which combines high injection efficiency (>90%) with a superior passivation of QDs.

# Ultrabright Fluorescent Silica Nanoparticles Embedded with Conjugated Oligomers and Their Application in Latent Fingerprint Detection\_2017

We have developed a simple approach for the large-scale synthesis of water-soluble green carbon nanodots (G-dots) from many kinds of large food waste-derived sources. About 120 g of G-dots per 100 kg of food waste can be synthesized using our simple and environmentally friendly synthesis approach. The G-dots exhibit a high degree of solubility in water because of the abundant oxygen-containing functional groups around their surface. The narrow band of photoluminescence emission (400–470 nm) confirms that the size of the G-dots (∼4 nm) is small because of a similar quantum effects and emission traps on the surfaces. The G-dots have excellent photostability; their photoluminescence intensity decreases slowly (∼8%) under continuous excitation with a Xe lamp for 10 days. We carried out cell viability assay to assess the effect of cytotoxicity by introducing G-dots in cells such as Chinese hamster ovary cells (CHO-K1), mouse muscle cells (C2C12), and African green monkey kidney cells (COS-7), up to a concentration of 2 mg mL–1 for 24 h. Due to their high photostability and low cytotoxicity, these G-dots are excellent probes for in vitro bioimaging. Moreover, the byproducts (not including G-dots) of G-dot synthesis from large food-waste derived sources promoted the growth and development of seedlings germinated on 3DW-supplemented gauze. Because of the combined advantages of green synthesis, high aqueous stability, high photostability, and low cytotoxicity, the G-dots show considerable promise in various areas, including biomedical imaging, solution state optoelectronics, and plant seed germination and/or growth.

# Balancing Electron Transfer and Surface Passivation in Gradient CdSe/ZnS Core–Shell Quantum Dots Attached to ZnO\_2013

In the search for improved materials for photoelectrochemical water splitting, it has become important to identify new classes of semiconductor materials that may serve as improved photocathodes. To this end, p-type AgRhO2 has been synthesized and tested as a photocathode for water splitting. The AgRhO2 photocathode is found to exhibit excellent photocatalytic capability for reducing protons to H2 across a wide range of pH values with nearly 100% faradaic efficiency and good photostability. Polycrystalline AgRhO2 electrodes exhibit strong preferred c-axis orientation, resulting in anisotropic conductivity, evident from resistivity measurements. AgRhO2 photocathodes are found to provide improved performance and photostability when compared to prior work using a p-CuRhO2 electrode. Enhanced performance is in part attributed to the unusual degree of c-axis orientation found in this material. In addition, there is a significantly lower kinetic barrier for H2 production at the AgRhO2 interface.

# Photoluminescent Green Carbon Nanodots from Food-Waste-Derived Sources: Large-Scale Synthesis, Properties, and Biomedical Applications\_2014

Effective long-term monitoring of tumor growth is significant for the evaluation of cancer therapy. Aggregation-induced emission-active near-infrared (NIR) fluorescent organic nanoparticles (TPFE-Rho dots) are designed and synthesized for long-term in vitro cell tracking and in vivo monitoring of tumor growth. TPFE-Rho dots display the advantages of NIR fluorescent emission, large Stokes shift (∼180 nm), good biocompatibility, and high photostability. In vitro cell tracing studies demonstrate that TPFE-Rho dots can track SK-Hep-1 cells over 11 generations. In vivo optical imaging results confirm that TPFE-Rho dots can monitor tumor growth for more than 19 days in a real-time manner. This work indicates that TPFE-Rho dots could act as NIR fluorescent nanoprobes for real-time long-term in situ in vivo monitoring of tumor growth.

# Stable Hydrogen Evolution from an AgRhO2 Photocathode under Visible Light\_2018

The fluorescence of tetraphenylethylene (TPE), an archetypal luminogen, is induced by restriction of intramolecular rotation (RIR). TPE was grafted with palmitic acid (PA) onto a hydrophilic peptide to yield a cell membrane tracker named TR4. TR4 was incorporated into liposomes, where it showed significant RIR characteristics. When cells were incubated with TR4, cytoplasmic membranes were specifically labeled. TR4 shows excellent photostability and low cytotoxicity.

# Aggregation-Induced Emission-Active Near-Infrared Fluorescent Organic Nanoparticles for Noninvasive Long-Term Monitoring of Tumor Growth\_2018

Quantum dots (QDs) are generally used for the conventional fluorescence detection. However, it is difficult for the QDs to be applied in time-resolved fluorometry due to their short-lived emission. In this paper, high-quality Mn-doped ZnSe QDs with long-lived emission were prepared using a green and rapid microwave-assisted synthetic approach in aqueous solution. Fluorescence lifetime of the Mn-doped ZnSe QDs was extended as long as 400 μs, which was 10 000 times higher than that of conventional QDs such as CdS, CdSe, and CdTe. The QDs exhibited an excellent photostability over 35 h under continuous irradiation at 260 nm. Capped with mercaptopropionic acid (MPA), the Mn-doped ZnSe QDs were used for the time-resolved fluorescence detection of 5-fluorouracil (5-FU) with the detection limit of 128 nM. The relative standard deviation for seven independent measurements of 1.5 μM 5-FU was 3.8%, and the recovery ranged from 93% to 106%. The results revealed that the Mn-doped ZnSe QDs could be a good candidate as a luminescence probe for highly sensitive time-resolved fluorometry.

# Cell Membrane Tracker Based on Restriction of Intramolecular Rotation\_2014

The current contribution aims to prepare a family of nitrofurantoin (NF) co-crystals and to investigate the ability of these co-crystals in enhancing the photostability and clinically relevant physicochemical properties of NF. Accordingly, supramolecular synthesis of the antibiotic drug NF with the co-formers 3-aminobenzoic acid (3ABA), 4-aminobenzoic acid (4ABA), urea, 4-hydroxybenzamide (4HBAM), phenazine (PHEN), melamine (MELA), 4,4′-bipyridine (BIPY) and 1,2-bis(4-pyridyl ethane) (BIPE) have produced five co-crystals and three co-crystal hydrates. Solid-state physical characterizations have been conducted by powder X-ray diffraction (PXRD), single crystal X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), hot-stage microscopy (HSM) and spectroscopy (Raman and 1H NMR). Crystal structures have been analyzed based on homo- and heterosynthons. Six out of eight multicomponent crystals are primarily stabilized by heterosynthons, whereas the remaining two co-crystals (NF-4ABA and NF-UREA) contain homosynthons. Notably, thermal analysis of co-crystal hydrates showed high thermal stability (∼166 °C, NF-MELA-H2O) or upon dehydration provided new anhydrous co-crystals, NF-BIPY and NF-BIPE in a 2:1 molar ratio. Physicochemical properties such as aqueous solubility, intrinsic dissolution rate and photostability have been investigated for NF-3ABA, NF-4ABA, NF-UREA and NF-4HBAM. Co-crystals display enhanced physicochemical properties as compared to that of NF: NF-4HBAM > NF-3ABA > NF-4ABA > NF-UREA > NF (β-form). The results suggest that co-crystals can be a viable alternative for improving the biopharmaceutical properties of API.

# Manganese-Doped ZnSe Quantum Dots as a Probe for Time-Resolved Fluorescence Detection of 5-Fluorouracil\_2011

Single molecule tracking in live cells is the ultimate tool to study subcellular protein dynamics, but it is often limited by the probe size and photostability. Because of these issues, long-term tracking of proteins in confined and crowded environments, such as intracellular spaces, remains challenging. We have developed a novel optical probe consisting of 5 nm gold nanoparticles functionalized with a small fragment of camelid antibodies that recognize widely used green fluorescent proteins (GFPs) with a very high affinity, which we call GFP-nanobodies. These small gold nanoparticles can be detected and tracked using photothermal imaging for arbitrarily long periods of time. Surface and intracellular GFP-proteins were effectively labeled even in very crowded environments such as adhesion sites and cytoskeletal structures both in vitro and in live cell cultures. These nanobody-coated gold nanoparticles are probes with unparalleled capabilities; small size, perfect photostability, high specificity, and versatility afforded by combination with the vast existing library of GFP-tagged proteins.

# Co-Crystals and Co-Crystal Hydrates of the Antibiotic Nitrofurantoin: Structural Studies and Physicochemical Properties\_2012

Nanoemulsions (NEs) are biocompatible lipid nanoparticles composed of an oily core stabilized by a surfactant shell. It is acknowledged that the surface decoration with poly(ethylene glycol), through the use of nonionic surfactants, confers high stealth in biological medium with reduced nonspecific interactions. Tracking individual NE by fluorescence microscopy techniques would lead to a better understanding of their behavior in cells and thus require the development of bright single particles with enhanced photostability. However, the understanding of the relationship between the physicochemical properties and chemical composition of the NEs, on the one hand, and its fluorescence properties of encapsulated dyes, on the other hand, remains limited. Herein, we synthesized three new dioxaborine barbituryl styryl (DBS) dyes that displayed high molar extinction coefficients (up to 120 000 M–1 cm–1) with relatively low quantum yields in solvents and impressive fluorescence enhancement when dissolved in viscous oils (up to 0.98). The reported screening of nine different oils allowed disclosing a range of efficient “oil/dye” couples and understanding the main parameters that lead to the brightest NEs. We determine vitamin E acetate/DBS-C8 as the representative most efficient couple, combining high dye loading capabilities and low aggregation-induced quenching, leading to <50 nm ultrabright NEs (with brightness as high as 30 × 106 M–1 cm–1) with negligible dye leakage in biological media. Beyond a comprehensive optical and physicochemical characterization of fluorescent NEs, cellular two-photon excitation imaging was performed with polymer-coated cell penetrating NEs. Thanks to their impressive brightness and photostability, NEs displaying different charge surfaces were microinjected in HeLa cells and were individually tracked in the cytosol to study their relative velocity.

# A Highly Specific Gold Nanoprobe for Live-Cell Single-Molecule Imaging\_2013

A newly synthesized reaction-based two-photon (TP) fluorescence imaging probe, 9-butyltriphenylphosphoniumacylamino-2,7-dibenzothiazolineflurene (MF-DBZH), composed of a superoxide anion (O2•–) responsive group and a mitochondria-targeted site, has been shown to have high selectivity toward mitochondrial O2•– fluxes. The fluorescence intensity of MF-DBZH responds proportionally to changes in O2•– concentrations. Moreover, MF-DBZH was proved to be insensitive toward pH changes and has high photostability. Favorable features of this probe also include convenient cell loading, easy staining of both cells and small animals, and excellent biocompibility. Most importantly, MF-DBZH gives reliable TP fluorescent signal to changes of O2•– levels in vivo.

# Optimizing the Fluorescence Properties of Nanoemulsions for Single Particle Tracking in Live Cells\_2019

A novel surface architecture was developed to generate biocompatible and stable photoswitchable quantum dots (psQDs). Photochromic diheteroarylethenes, which undergo thermally stable photoconversions between two forms with different spectral properties in organic solvents, were covalently linked to an amphiphilic polymer that self-assembles with the lipophilic chains surrounding commercial hydrophobic core−shell CdSe/ZnS QDs. This strategy creates a small (∼7 nm diameter) nanoparticle (NP) that is soluble in aqueous medium. The NP retains and even enhances the desirable properties of the original QD (broad excitation, narrow emission, photostability), but the brightness of its emission can be tailored by light. The modulation of emission monitored by steady-state and time-resolved fluorescence was 35−40%. The psQDs exhibit unprecedented photostability and fatigue resistance over at least 16 cycles of photoconversion.

# Mitochondria-Targeted Reaction-Based Two-Photon Fluorescent Probe for Imaging of Superoxide Anion in Live Cells and in Vivo\_2013

Recent reports have shown enhanced fluorescence for fluorophores in close proximity to chemically deposited silver islands or colloids. To expand the usefulness of metal-enhanced fluorescence we tested fractal silver structures formed on, or near, silver electrodes by passage of electric currents. The emission intensity of fluorescein-labeled human serum albumin (FITC-HSA) was enhanced over 100-fold when adsorbed to the fractal silver structures as compared to glass. The amplitude-weighted lifetime is dramatically reduced to near 3 ps. Enhanced fluorescence was shown to result in selective observation of FITC-HSA over a fluorophore not attached to the silver surface. And finally, photostability measurements indicate 160-fold more photons are detectable from FITC-HSA on the fractal silver surface. These results suggest the use of in situ generated silver structures for metal-enhanced fluorescence.

# Photoswitchable Water-Soluble Quantum Dots: pcFRET Based on Amphiphilic Photochromic Polymer Coating\_2011

Quantum dots (QDs) are fluorescent nanoparticles with unique photophysical properties that enable them to potentially replace traditional organic dyes and fluorescent proteins in various bioimaging applications. However, the inherent toxicity of their cores based on cadmium salts limits their widespread biomedical use. We have developed a novel nanocomposite polymer emulsion based on polyhedral oligomeric silsesquioxane poly(carbonate-urea) urethane (POSS–PCU) that can be used to coat quantum dots to nullify their toxicity and enhance photostability. Here we report the synthesis and characterization of a novel POSS–PCU nanocomposite polymer emulsion and describe its application for coating QDs for biological application. The polymer was synthesized by a process of emulsion polymerization and formed stable micelles of ∼33 nm in diameter. CdTe/CdS/ZnS QDs were efficiently stabilized by the polymer emulsion through encapsulation within the polymer micelles. Characterization studies showed no significant change in the unique photophysical properties of QDs after coating. The polymer was biocompatible to HepG2, HUVECs, and mouse skeletal muscle cells at 2.5% after 24 h exposure on in vitro testing. Polymer encapsulated QDs showed enhanced photostability on exposure to high degrees of UV irradiation and air as well as significantly reduced cytotoxicity on exposure to HepG2 cells at 30 μg/mL for 24 h. We have therefore concluded that the POSS–PCU polymer emulsion has the potential to make a biocompatible and photostable coating for QDs enabling a host of biomedical applications to take this technology to the next level.

# Enhanced Fluorescence from Fluorophores on Fractal Silver Surfaces\_2003

The construction of coronenes using simple building blocks is a challenging task. In this work, triphenylene was used as a building block to construct functionalized coronenes, and their solid structures and optoelectronic properties were investigated. The single crystal structures showed that coronenes have different packing motifs. Their good solubility and photostability make them potential solution-processable candidates for organic devices.

# Novel POSS–PCU Nanocomposite Material as a Biocompatible Coating for Quantum Dots\_2015

The synthesis, purification, and spectral properties of new dithienothiophene-based fluorescent dyes with a terminal alkyl bromide group are described. The bromides were easily converted to isothiocyanates and N-succinimidyl esters by appropriate chemical transformations with sodium thiocyanate or N-hydroxysuccinimide. The new fluorophores exhibited intense fluorescence emission and high photostability. Their suitability for bioanalytical applications was evaluated through conjugation with amine-reactive polystyrene microspheres and IgG anti-CD3 monoclonal antibody.

# Functionalized Coronenes: Synthesis, Solid Structure, and Properties\_2012

Peptides and proteins have diverse ultraviolet (UV) photoreaction pathways that can be activated by the energy of the UV photons absorbed. Simple light sources such as lamps are conventionally used to study these photoreactions in solution. This work provides a proof of concept that femtosecond laser technology can function as a highly potent UV source in rapidly conducting UV photostability studies of peptides. Correspondingly, sufficient quantities of photoproducts were generated in 1 min or less, allowing for identification of known and new photomodifications in the therapeutic peptides somatostatin-14 and arginine vasopressin. Identical photoproducts were also generated with a conventional continuous source. The major modifications included N-formylkynurenine, a cross-link between Trp and Phe, a Tyr product with an NH3 loss, and disruption of an unstable disulfide bond into a complex mixture of a trisulfide bond and multiple scrambled dimeric products. In conclusion, femtosecond lasers are extremely useful to drive fast UV-induced reactions for high throughput screening of photostability and modifications in amino acid polymers.

# Synthesis of Photostable Amine-Reactive Fluorescent Dyes by Postsynthetic Conversion of Bromide Dithienothiophene Derivatives\_2007

The fluorescence of individual light-harvesting 2 complexes from Rhodopseudomonasacidophila has been observed by confocal microscopy in a temperature range between 300 and 7 K. Under ambient conditions, changes in the polarization of the fluorescence emission of single complexes on a time scale from milliseconds to seconds are found. In the temperature range between 250 and 100 K most complexes emit fluorescence with a temporally stable linear fluorescence polarization. At temperatures below 70 K, spectral diffusion is found to dominate the dynamics of the fluorescence intensity and polarization. The increase in photostability of single complexes at low temperature allows the detection of fluorescence emission spectra of single complexes. A marked variation in the shape and the position of the spectra is found. The results are discussed by considering static and dynamic disorder within the B850 aggregate of the light-harvesting complexes.

# Characterization of Ultraviolet Photoreactions in Therapeutic Peptides by Femtosecond Laser Catalysis and Mass Spectrometry\_2019

Ternary terbium complexes were fully encapsulated and uniformly distributed into the channels of unmodified and modified mesoporous molecule sieves of SBA-15 and characterized by transmission electron micrographs (TEM), Fourier transform infrared spectroscopy (FTIR), ultraviolet−visible (UV−vis) absorption spectra, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and elemental analysis. The luminescent properties for the encapsulated complexes were systematically studied in contrast to the pure complexes, including excitation and emission spectra, fluorescence dynamics, photostability under UV exposure, and the temperature dependence of intensity and lifetime. The results indicate that the excitation bands assigned to the π−π\* electron transition of the ligands for Tb complexes encapsulated in SBA-15 were split into different components due to decreased symmetry and disappeared at long wavelengths. Owing to suppressed vibration transitions, the outer quantum efficiency of the 5D4-7FJ (J = 0−5) emissions was enhanced largely in comparison to the pure complexes. In addition, the photostability and thermostability of the emissions were also improved considerably.

# Spectroscopy on Single Light-Harvesting Complexes at Low Temperature\_1999

Fluorescent sensors with advantages of excellent sensitivity, rapid response, and easy operation are emerging as powerful tools in environmental monitoring, biological research, and disease diagnosis. However, conventional fluorophores featured with π-planar structures usually suffer from serious self-quenching in the aggregated state, poor photostability, and small Stokes’ shift. In contrast to conventional aggregation-caused quenching (ACQ) fluorophores, the newly emerged aggregation-induced emission fluorogens (AIEgens) are featured with high emission efficiency in the aggregated state, which provide unique opportunities for various sensing applications with advantages of high signal-to-noise ratio, strong photostability, and large Stokes’ shift. In this review, we will first briefly give an introduction of the AIE concept and the turn-on sensing principles. Then, we will discuss the recent examples of AIE sensors according to types of analytes. Finally, we will give a perspective on the future developments of AIE sensors. We hope this review will inspire more endeavors to devote to this emerging world.

# Improved Photoluminescence Properties of Ternary Terbium Complexes in Mesoporous Molecule Sieves\_2006

Synthesis and physical characterizations of a series of 7,14-diaryl-substituted zethrene diimides (ZDIs) bearing different substituents (alkyl chain, oligoethyleneglycol ether chain, and aryl group) at the imide sites as well as at the bay regions are described in this study. The synthesis takes advantage of Pd-catalyzed cyclodimerization reaction that allows construction of zethrene core and substitution at the bay region in one single step. The partially cyclized ZDI is also separated as a minor product. The carboxylic acid group is introduced to the bay region for the purpose of further bioconjugation. The photophysical properties, electrochemical properties, and photostability of these ZDI dyes are investigated with UV/vis spectroscopic measurements, cyclic voltammetry measurements, and photoirradiation tests. These dyes exhibit tunable photophysical properties in the far-red spectral region with moderate fluorescent quantum yields and good stability. The enhanced stability as compared to the parent zethrene and the 7,14-substituted zethrenes can be attributed to the electron-withdrawing effect of the imide groups and the kinetic blocking of the most reactive sites at the bay region.

# Fluorescent Sensors Based on Aggregation-Induced Emission: Recent Advances and Perspectives\_2017

It is of a primary importance to realize the intrinsic emission from the inner carbogenic cores of carbon dots (CDs). In this work, CDs with three emission centers were synthesized by a microwave-assisted method using phloroglucinol as a precursor. The emission of these three centers has been identified as originating from molecular fluorophores, surface states of CDs, and the intrinsic CD core state. The emission from molecular fluorophores and from the surface state of CDs exhibited a weak photostability and could be photobleached as a result of UV laser irradiation. The emission from the intrinsic state of the inner carbogenic core has been found to be stable against photobleaching. On the basis of this difference in photostability, we demonstrate how the surface of CDs can be deoxidized under prolonged UV irradiation, resulting in a narrow intrinsic emission with a photoluminescence quantum yield of 17%.

# 7,14-Diaryl-Substituted Zethrene Diimides as Stable Far-Red Dyes with Tunable Photophysical Properties\_2013

Facile synthetic routes to a new class of red α-benzo-fused BOPHYs with 6,5,6,6,5,6-hexacyclic fused rings and β-thiophene-fused BOPHYs with 5,5,6,6,5,5-hexacyclic fused rings are presented. These dyes were characterized by NMR spectroscopy, HRMS, X-ray structure analysis, cyclic voltammetry, and optical measurements. Compared to parent BOPHY, significant red-shifts in the absorption (up to 600 nm in solution) and emission (up to 648 nm in solution and 717 nm in solid state), as well as high chemical stability and photostability, were found for these aromatic-ring-fused BOPHY dyes. As shown in cyclic voltammetry and DFT calculations, the aromatic ring fusions induced significantly increased HOMO energy levels, giving effective expansion of π-conjugation over these BOPHY dyes. These new molecular skeletons would be promising candidates for various applications in light of their unique structure and attractive photophysical properties.

# Realization of the Photostable Intrinsic Core Emission from Carbon Dots through Surface Deoxidation by Ultraviolet Irradiation\_2019

We have synthesized a red biarsenical fluorescent probe, AsCy3, with good photostability, low pH sensitivity, high absorbance, and good quantum yield. It is directed specifically to a small tetracysteine peptide binding motif, Cy3TAG (CysCysLysAlaGluAlaAlaCysCys), in the presence of other tetracysteine tags. This new probe provides a FRET partner to biarsenical dye FlAsH, making this discovery an important step toward a whole toolkit of colored probes directed to different small peptide motifs.

# Aromatic Ring Fused BOPHYs as Stable Red Fluorescent Dyes\_2016

Low-molecular-weight organic molecules, such as coumarins and stilbenes, are used commercially as fluorescent whitening agents (FWAs) to mask photoyellowing and to brighten colors in fabrics. FWAs achieve this by radiating extra blue light, thus changing the hue and also adding to the brightness. However, organic FWAs can rapidly photodegrade in the presence of ultraviolet (UV) radiation, exacerbating the yellowing process through a reaction involving singlet oxygen species. Inorganic nanoparticles, on the other hand, can provide a similar brightening effect with the added advantage of photostability. We report a targeted approach in designing new inorganic silicon- and germanium-based nanoparticles, functionalized with hydrophilic (amine) surface terminations as novel inorganic FWAs. When applied on wool, by incorporation in a sol–gel Si matrix, the inorganic FWAs improved brightness properties, demonstrated enhanced photostability toward UV radiation, especially the germanium nanoparticles, and also generated considerably lower levels of reactive oxygen species compared to a commercial stilbene-based organic FWA, Uvitex NFW.

# A Red Cy3-Based Biarsenical Fluorescent Probe Targeted to a Complementary Binding Peptide\_2007

There is little information about pesticide photostability on plants, especially when considering the effects of the formulation. We evaluated the photostability of a herbicide, mesotrione, on wax films. These surfaces are good systems to mimic the outer layer of the leaf. Within the range of recommended agricultural rates, pure mesotrione half-life on cuticular wax films was between 100 and 160 min. Formulated, the phototransformation rate was multiplied by a factor of 4.8. We assume that the acceleration is mainly due to the surfactants, agents that allow a better spreading of the active ingredient at the leaf surface. Since mesotrione photolysis is a fast process on wax films, we can assume that this process would be significant in the field after treatment.

# Silicon and Germanium Nanoparticles with Tailored Surface Chemistry as Novel Inorganic Fiber Brightening Agents\_2013

We have synthesized a red biarsenical fluorescent probe, AsCy3, with good photostability, low pH sensitivity, high absorbance, and good quantum yield. It is directed specifically to a small tetracysteine peptide binding motif, Cy3TAG (CysCysLysAlaGluAlaAlaCysCys), in the presence of other tetracysteine tags. This new probe provides a FRET partner to biarsenical dye FlAsH, making this discovery an important step toward a whole toolkit of colored probes directed to different small peptide motifs.

# Photobleaching Efficiency Parallels the Enhancement of Membrane Damage for Porphyrazine Photosensitizers\_2019

Novel organosilica nanoparticles made of 3-mercaptopropyltrimethoxysilane as the single silica source (MPS NPs) have been synthesized successfully by using a Stöber method. The MPS NPs were well dispersed in solution and have unique surface properties such as thiol residues on the surface and reduced zeta potential compared with the nanoparticles made of tetraethoxysilane. The MPS NPs with fluorescent dye were synthesized by a method that deposited fluorescent dye on the silica network. The resulting MPS NPs with fluorescence were bright, nonaggregated in solution, and photostable. The fluorescence intensity and photostability of fluorescent MPS NPs were sufficient for detection as a single fluorescent particle using flow cytometry and fluorescence microscopy. Protein-modified MPS NPs were prepared easily by absorption and by maleimide coupling. In this paper, we demonstrate the usefulness of MPS NPs and their surface properties and discuss their advantages for biological applications.

# Effect of a Spreading Adjuvant on Mesotrione Photolysis on Wax Films\_2009

Surface plasmon coupled fluorescence (SPCF) and metal enhanced fluorescence (MEF) over a broad wavelength range from UV to NIR are demonstrated from 20 nm thin indium films. Steady-state and time-resolved fluorescence measurements of fluorophores deposited on the indium thin films indicate enhancement of the fluorescence intensity along with decreases in decay times, both in MEF and SPCF modes, accompanied by an increase in photostability. MEF was found to be more pronounced for the red emission dye with respect to a blue emission dye. A completely p-polarized directional emission for three fluorophores from a hemicylindrical prism at 44° indicates surface plasmons couple with the near field dipoles at the interface of the indium-sample. The evanescent waves generated at the interface are calculated to penetrate more deeply for longer wavelength excitation with respect to shorter wavelengths, and the penetration depth nearly doubles in comparison to that of the widely used silver thin films. As an application, indium thin films have been used for intrinsic protein chromophore (tryptophan) fluorescence detection. Nearly a 3.5-fold enhancement of intrinsic protein fluorescence along with a decreased decay time and increase in photostability were observed with SPCF. Subsequently, indium thin films can be utilized as a single assay platform in surface plasmon fluorescence spectroscopy (SPFS) over a broad spectral range and can potentially be a much better choice than other metallic thin films.

# Synthesis and Characterization of Organosilica Nanoparticles Prepared from 3-Mercaptopropyltrimethoxysilane as the Single Silica Source\_2007

Photoinduced electron transfer in fluorescent proteins from the GFP family can be regarded either as an asset facilitating new applications or as a nuisance leading to the loss of optical output. Photooxidation commonly results in green-to-red photoconversion called oxidative redding. We discovered that yellow FPs do not undergo redding; however, the redding is restored upon halide binding. Calculations of the energetics of one-electron oxidation and possible electron transfer (ET) pathways suggested that excited-state ET proceeds through a hopping mechanism via Tyr145. In YFPs, the π-stacking of the chromophore with Tyr203 reduces its electron-donating ability, which can be restored by halide binding. Point mutations confirmed that Tyr145 is a key residue controlling ET. Substitution of Tyr145 by less-efficient electron acceptors resulted in highly photostable mutants. This strategy (i.e., calculation and disruption of ET pathways by mutations) may represent a new approach toward enhancing photostability of FPs.

# UV to NIR Surface Plasmon Coupled and Metal-Enhanced Fluorescence Using Indium Thin Films: Application to Intrinsic (Label-less) Protein Fluorescence Detection\_2011

A novel rhodamine based probe with a unique six-membered spirocycle was rationally designed for detection of Hg2+ with greatly improved selectivity, sensitivity, and photostability. The probe has been shown to be suitable for Hg2+ imaging in living cells and mapping Hg2+ distribution in living cell–EPS–mineral aggregates under anoxic conditions.

# Turning On and Off Photoinduced Electron Transfer in Fluorescent Proteins by π-Stacking, Halide Binding, and Tyr145 Mutations\_2016

Surface-enhanced Raman scattering (SERS) tags can be utilized as optical labeling nanoprobes similar to fluorescent dyes and quantum dots for bioimaging with additional advantages of fingerprint vibrational signals as unique optical codes and ultranarrow line widths for multiplexing. However, the development of the SERS imaging technique is much less well-established compared to the devlopment of fluorescence imaging mainly because of speed limitations. An effective strategy for improving the SERS imaging speed and simultaneously maintaining the photostability of SERS tags has not, to the best of our knowledge, been reported. In this work, mesoporous silica- (MS-) coated gap-enhanced Raman tags (GERTs) were designed with built-in Raman reporters for off-resonance near-infrared laser excitation and reduced photothermal effects, leading to ultraphotostability during laser irradiation. Additionally, they achieve large amplification of Raman signals by combining the chemical (CHEM) and electromagnetic (EM) enhancement effects due to the subnanometer core–shell junction, so SERS imaging can be performed in a dramatically reduced duration. With these unique structural and optical advantages, MS GERTs exhibit high storage, pH, serum, and photostabilities; strong Raman enhancements; and favorable biocompatibility. Therefore, MS GERTs achieve long-term cell imaging that can last for 30 min without being photobleached and also maintain decent imaging effects. Furthermore, MS GERTs enable continuous and stable imaging in living tissues for more than 30 min. With these advantages, MS GERTs might potentially have more biomedical applications.

# Six-Membered Spirocycle Triggered Probe for Visualizing Hg2+ in Living Cells and Bacteria–EPS–Mineral Aggregates\_2013

The mucoadhesive nanoparticles (NPs) for oral delivery of coenzyme Q10 (CoQ10) were prepared using natural mucoadhesive polysaccharides, chitosan (CS), and dextran sulfate sodium salt (DS) in order to improve the solubility, cellular uptake, and thermo- and photostability of CoQ10. CoQ10-loaded NPs were prepared in the range of 340–450 nm with an entrapment efficiency of 60–98%. The mucoadhesiveness and cellular uptake of NPs were evaluated by measuring the amount of mucin adsorbed on NPs and CoQ10 absorbed in Caco-2 cells, respectively. CS/DS NPs had higher mucoadhesive strength than CS/sodium triphosphate pentabasic NPs (control group). Moreover, the solubility, cellular uptake, thermo- and photostability of CS/DS NPs were significantly improved compared with non-nanoencapsulated free CoQ10. Particularly, CS/DS NPs prepared with 0.5 mg/mL of CS and DS produced the highest mucoadhesiveness, solubility, cellular uptake, and cellular antioxidant activity. Thus, mucoadhesive CS/DS NPs may be an effective oral delivery platform for improving bioavailability of CoQ10.

# Ultraphotostable Mesoporous Silica-Coated Gap-Enhanced Raman Tags (GERTs) for High-Speed Bioimaging\_2017

Mitochondria are crucial in the process of oxidative metabolism and apoptosis. Their morphology is greatly associated with the development of certain diseases. For specific and long-term imaging of mitochondrial morphology, we synthesized a new mitochondria-targeted near-infrared (NIR) fluorescent probe (TPE–Xan–In) by incorporating TPE with a NIR merocyanine skeleton (Xan–In). TPE–Xan–In displayed both absorption (660 nm) and emission peaks (743 nm) in the NIR region. Moreover, it showed aggregation-induced emission properties at neutral pH and specifically illuminated mitochondria with good biocompatibility, superior photostability, and high tolerance to mitochondrial membrane potential changes. With a pH-responsive unit, hydroxyl xanthene (Xan), the probe exhibited a pH-sensitive fluorescence emission in the range of pH 4.0–7.0, which indicated its potential in long-term tracking of pH and morphology changes of mitochondria in the biomedical research studies.

# Preparation and Characterization of Mucoadhesive Nanoparticles for Enhancing Cellular Uptake of Coenzyme Q10\_2017

Pyrethroids, in general, have a high degree of activity as insecticides while showing a low mammalian toxicity. The natural pyrethroids cannot be used commercially to protect agricultural crops mainly because of their high cost and their poor photostability. The synthesis of 3-phenoxybenzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (NRDC 143) has been reported (1). This material has high insecticidal activity and low mammalian toxicity. It also has greater photostability than the natural pyrethroids.  
NRDC 143 has been prepared from its corresponding ethyl ester. Acid hydrolysis of ethyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate 1 formed 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid 2. Treatment of 2 with thionyl chloride gave the corresponding acid chloride 3, in an 80% overall yield from 1. Treatment of 3 with 3-phenoxybenzyl alcohol formed the desired NRDC 143.  
Compound 1 has been prepared by the method of Farkas (2). Condensation of chloral with isobutylene gave 1,1,1-trichloro-2-hydroxy-4-methyl-4-pentene 4 and its isomeric 3-pentene 13. Acetylation of 4 and 13 with a mixture

# Photostable pH-Sensitive Near-Infrared Aggregation-Induced Emission Luminogen for Long-Term Mitochondrial Tracking\_2019

The extent of lipid packing is one of the key physicochemical features of biological membranes and is involved in many membrane processes. Polarity sensitive fluorescent probes are commonly used tools to measure membrane lipid packing in both artificial and biological membranes. In this paper, we have systematically compared eight different probes to measure membrane lipid ordering. We investigated how these probes behave in small unilamellar liposomes, phase-separated giant unilamellar vesicles, cell-derived giant plasma membrane vesicles, and live cells. We have tested the order sensitivity of a variety of measurable parameters, including generalized polarization, peak shift, or intensity shift. We also investigated internalization and photostability of the probes to assess probe potential for time-lapse live cell imaging. These results provide a catalogue of properties to facilitate the choice of probe according to need.

# Novel Routes to 1,1-Dichloro-4-methyl-1,4-pentadiene and 1,1-Dichloro-4-methyl-1,3-pentadiene\_1977

Fluorescent proteins have become an invaluable tool in cell biology. The green fluorescent protein variant EGFP is especially widely applied. Use of fluorescent proteins, including EGFP, however can be hindered by inefficient protein folding, resulting in protein aggregation and reduced fluorescence. This is especially profound in prokaryotic cells. Furthermore, EBFP, a blue fluorescent variant of EGFP, is rarely used because of its dim fluorescence and fast photobleaching. Thus, efforts to improve properties such as protein folding, fluorescence brightness, and photostability are important. Strongly enhanced green fluorescent (SGFP2) and strongly enhanced blue fluorescent (SBFP2) proteins were created, based on EGFP and EBFP, respectively. We used site-directed mutagenesis to introduce several mutations, which were recently shown to improve the fluorescent proteins EYFP and ECFP. SGFP2 and SBFP2 exhibit faster and more efficient protein folding and accelerated chromophore oxidation in vitro. For both strongly enhanced fluorescent proteins, the photostability was improved 2-fold and the quantum yield of SBFP2 was increased 3-fold. The improved folding efficiency reduced the extent of protein aggregation in Escherichia coli, thereby increasing the brightness of bacteria expressing SGFP2 7-fold compared to the brightness of those expressing EGFP. Bacteria expressing SBFP2 were 16-fold more fluorescent than those expressing EBFP. In mammalian cells, the improvements were less pronounced. Cells expressing SGFP2 were 1.7-fold brighter than those expressing EGFP, which was apparently due to more efficient protein expression and/or chromophore maturation. Mammalian cells expressing SBFP2 were 3.7-fold brighter than cells expressing EBFP. This increase in brightness closely resembled the increase in intrinsic brightness observed for the purified recombinant protein. The increased maturation efficiency and photostability of SGFP2 and SBFP2 facilitate detection and extend the maximum duration of fluorescence imaging.

# Measuring Lipid Packing of Model and Cellular Membranes with Environment Sensitive Probes\_2014

As the critical property of the organic dye, the energy level determines the thermodynamic possibilities and the efficiencies of multiple interfacial charge-transfer processes in dye-sensitized solar cells. Thus, a suitable energy level is highly required, and selective energy control becomes a quite important and systemic objective. Herein, a novel planar carbazole unit, which is synthesized through simple aryl immobilization, is applied as the donor segment in the D–A−π–A organic dye. The considerable dihedral angle between benzene and carbazole is almost eliminated, thus resulting in effective improvement of molecular planarity. As the planarity of donor segment enhances, the highest occupied molecular orbital level of the dye increases, whereas its lowest unoccupied molecular orbital level remains around the same value, with respect to the twisted dye. Besides, with good molecular planarity, the interfacial charge-transfer processes, including charge injection, charge recombination, and dye regeneration, are efficiently improved. Consequently, the optimization of molecular planarity can selectively control the energy level of the dye, while multiple interfacial charge-transfer processes can also be finely optimized, providing a reasonable strategy to develop an efficient organic sensitizer with long-term photostability.

# Improved Green and Blue Fluorescent Proteins for Expression in Bacteria and Mammalian Cells,\_2007

We have measured the absorption spectrum, the emission spectrum, the emission lifetime, and the photostability of fluorescein isothiocyanate (FITC) incorporated inside colloidal silica spheres as a function of the dye concentration in the spheres, while minimizing scattering effects. Six batches of stable, monodisperse particles were synthesized with FITC up to high densities of 0.03 M. At dye concentrations above 0.001 M, we observe a large red shift of 10 nm in the absorption and the emission spectra, as well as a strong reduction of the lifetime. At the same time, the photostability of the dye is considerably improved. These effects are caused by an increased energy transfer between the dye molecules as their concentration increases. Several excitation quenching models are examined, namely annihilation quenching, surface quenching, and a fractal distribution of quenchers. None of the models that assume a homogeneous distribution of FITC provide a sufficient explanation of the observed effects. It is suggested that the dye molecules tend to form clusters during the synthesis of the colloidal spheres. It is concluded that colloids with a low dye concentration are useful for photonic applications, whereas high dye concentrations are interesting for optical experiments in colloid science.

# Energy-Level Control via Molecular Planarization and Its Effect on Interfacial Charge-Transfer Processes in Dye-Sensitized Solar Cells\_2019

Photoswitchable fluorescent polymeric nanoparticles (PFPNs) with controllable molecular weight, high contrast, biocompatibility, and prominent photostability are highly desirable but still scarce for rewritable printing, super-resolution bioimaging, and rewritable data storage. In this study, novel amphiphilic BODIPY-based PFPNs with considerable merits are first synthesized by a facile one-pot RAFT-mediated miniemulsion polymerization method. The polymerization is performed by adopting polymerizable BODIPY and spiropyran derivatives, together with MMA as monomer, and mediated by utilizing biocompatible PEO macro-RAFT agent as both control agent and reactive stabilizer. The amphiphilic BODIPY-based PFPNs not only exhibit reversibly photoswitchable fluorescence properties under the alternative UV and visible light illumination through induced intraparticle fluorescence resonance energy transfer (FRET) but also display controllable molecular weight with narrow polydispersity index (PDI), high contrast of fluorescence, tunable energy transfer efficiency, good biocompatibility, excellent photostability, favorable photoreversibility, etc. The as-prepared PFPNs are successfully demonstrated for rewritable fluorescence patterning and high-contrast dual-color fluorescence imaging of living cells, implying its potential for rewritable data storage and broad biological applications in cell biology and diagnostics.

# Spectroscopy of Fluorescein (FITC) Dyed Colloidal Silica Spheres\_1999

A new strategy for fabricating water-dispersible Ag2Se quantum dots (QDs) is presented. A multidentate polymer (MDP) was synthesized and used as a capping agent for Ag2Se QDs. The MDP-capping Ag2Se QDs were synthesized in aqueous solution at room temperature, which are highly photoluminescent in a second near-infrared (NIR-II) biological window and possess good photostability. These readily prepared NIR-II fluorescent nanoprobes have great potential for biomedical applications, especially useful for in vivo imaging.

# Amphiphilic BODIPY-Based Photoswitchable Fluorescent Polymeric Nanoparticles for Rewritable Patterning and Dual-Color Cell Imaging\_2015

We have synthesized dual-lanthanide-chelated silica nanoparticles for potential use as labels in bioanalysis. A universal ligand 2,9-bis[N,N-bis(carboxymethyl)aminomethyl]-1,10-phenanthroline that could bind both Eu(III) and Tb(III) was covalently linked with 3-aminopropyl(triethoxy) silane to form silica nanoparticles in the presence of precisely controlled ratios of Eu(III)/Tb(III). The nanoparticles thus prepared could have specified ratios of luminescence intensities at two well-resolved emissions under a single-wavelength excitation. After comprehensive characterization with respect to their fluorescence lifetime, photostability, thermostability, and chelate leakage, a practical use of these nanoparticles was evaluated in a time-resolved immunofluorometric assay of human hepatitis B surface antigen. The results showed much increased sensitivity and quantification ranges than the enzyme-linked immunosorbent assay, demonstrating the suitability and advantages of these nanoparticles for bioassays.

# Aqueous Synthesis of Multidentate-Polymer-Capping Ag2Se Quantum Dots with Bright Photoluminescence Tunable in a Second Near-Infrared Biological Window\_2014

Europium (t-Eu) and gadolinium (t-Gd) β-diketonate complexes with photoactive t-bpete ligand, [Ln(btfa)3(t-bpete)(MeOH)] (Ln = Eu, Gd), where btfa– and t-bpete are 4,4,4-trifluoro-1-phenyl-1,3-butanedionate and trans-1,2-bis(4-pyridyl)ethylene, respectively, were synthesized, characterized by vibrational, absorption (reflectance) and photoluminescence spectroscopies and their crystal structure was determined using single-crystal X-ray diffraction. B3LYP calculations were performed to support the interpretation and rationalization of the experimental results. The complexes, under UV irradiation, do not display the typical photodegradation of the β-diketonate ligands exhibiting, in turn, an unprecedented photostability during, at least, 10 h. During UV-A exposure (>330 nm), the emission intensities of both complexes increase drastically (∼20 times), whereas for t-Eu the emission quantum yield is enhanced at least 30-fold. A mechanism based on a photoclick trans-to-cis isomerization of both t- and c-bpete moieties was proposed to explain the abnormal photostability of these compounds, either in solid state or in solution. The experimental and computational results are consistent with a photostationary state involving the trans-to-cis isomerization of the bpete ligand under continuous UV-A exposure, which thus diverts the incident radiation from other deleterious photochemical or photophysical processes that cause the typical photobleaching behavior of chelate lanthanide complexes. This shielding mechanism could be extended to other ligands permitting the design of new lanthanide-based photostable systems under UV exposure for applications in lighting, sensing, and displays.

# Dual-Lanthanide-Chelated Silica Nanoparticles as Labels for Highly Sensitive Time-Resolved Fluorometry\_2007

Facile aqueous synthesis of near-infrared Ag2Te quantum dots (QDs) and Ag2Te/ZnS core/shell QDs emitting in the second biological window is reported. The QD synthesis is based on a straightforward cation exchange process between CdTe QDs and Ag+ ions conducted in aqueous solution. The prepared Ag2Te QDs possess near-infrared emission ranging from 900 to 1300 nm and a quantum yield up to 2.1%. A ZnS shell was grown on the Ag2Te QD to further enhance the photoluminescence intensity with a quantum yield of 5.6%. These Ag2Te/ZnS core/shell QDs possess robust colloidal stability and photostability with minimum photoluminescence fluctuation upon incubation for 72 h in biological buffer or continuous laser excitation for 120 min. Also, These QDs possess small hydrodynamic size (∼7.6 nm) and are non-cytotoxic to human cells, which is ideal for optical bioimaging in the second biological window.

# Photo–Click Chemistry to Design Highly Efficient Lanthanide β-Diketonate Complexes Stable under UV Irradiation\_2013

A new oxygen sensor, compound 2, was synthesized through a chemical modification of a popularly used oxygen sensor of platinum(II)-5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin (PtTFPP). The new sensor compound 2 possesses four cross-linkable methacrylate functional moieties, enabling it to be polymerized and cross-linked with other monomers for polymer sensing film (also called membrane) preparation. Using this characteristic, compound 2 was covalently bonded to hydrophilic poly(2-hydroxyethyl methacrylate)-co-polyacrylamide (referred to as PHEMA to simplify) and hydrophobic polystyrene (PS) films. To better understand the advantages and disadvantages of chemical cross-linking approaches and the influence of polymer matrices on sensing performance, we physically incorporated PtTFPP into the same PHEMA and PS matrices to compare. Response to dissolved oxygen (DO), leaching of the sensor molecules from their matrices, photostability of the sensors, and response time to DO changes were studied. It was concluded that the chemical cross-linking of the sensor compound 2 in polymer matrices: (i) alleviated the leaching problem of sensor molecules that usually occurred in the physically doped sensing systems, and (ii) significantly improved sensors’ photostability. The PHEMA matrix was demonstrated to be more suitable for dissolved oxygen sensing than PS, because for the same sensor molecule, the oxygen sensitivity in PHEMA film was higher than that in PS and response time to DO change in the PHEMA film was faster than that in PS. It was the first time oxygen sensing films were successfully prepared using biocompatible hydrophilic PHEMA as a matrix, which does not allow leaching of the sensor molecules from the polymer matrix, has a faster response to DO changes than that of PS, and does not present cytotoxicity to human lung adenocarcinoma epithelial cells (A549). It is expected that the new sensor compound 2 and its similar compounds with chemical cross-linking characteristics can be widely applied to generate many interesting oxygen sensing materials for studying biological phenomena.

# Cation Exchange-Based Facile Aqueous Synthesis of Small, Stable, and Nontoxic Near-Infrared Ag2Te/ZnS Core/Shell Quantum Dots Emitting in the Second Biological Window\_2013

Fluorescent sensors suitable for dynamic measurement of intracellular pH (pHi) fluctuations should feature the following properties: feeble cytotoxicity, wide-pH range response, and strong fluorescence coupled with good photostability, which are still remaining scanty to date. Herein, by functionalizing fluorescent silicon nanoparticles (SiNPs) with pH-sensitive dopamine (DA) and pH-insensitive rhodamine B isothiocyanate (RBITC), we present the first demonstration of fluorescent SiNPs-based sensors, simultaneously exhibiting minimal toxicity (cell viability of treated cells remains above 95% during 24-h treatment), sensitive fluorescent response to a broad pH range (∼4–10), and bright fluorescence coupled with robust photostability (∼9% loss of fluorescence intensity after 40 min continuous excitation; in contrast, fluorescence of Lyso-tracker is rapidly quenched in 5 min under the same experiment conditions). Taking advantage of these merits, we further employ the resultant fluorescent SiNPs sensors for the detection of lysosomal pH change mediated by nigericin in live HeLa and MCF-7 cells in long-term (e.g., 30 min) manners. Interestingly, two consecutive stages, i.e., alkalization lag phase and logarithmic growth phase, are observed based on recording the whole process of pH change, offering important information for understanding the dynamic process of pHi fluctuations.

# A New Cross-Linkable Oxygen Sensor Covalently Bonded into Poly(2-hydroxyethyl methacrylate)-co-Polyacrylamide Thin Film for Dissolved Oxygen Sensing\_2010

Plasma membranes can sense the stimulations and transmit the signals from extracellular environment and then make further responses through changes in locations, shapes or morphologies. Common fluorescent membrane markers are not well suited for long time tracking due to their shorter retention time inside plasma membranes and/or their lower photostability. To this end, we develop a new bipolar marker, Mem-SQAC, which can stably insert into plasma membranes of different cells and exhibits a long retention time over 30 min. Mem-SQAC also inherits excellent photostability from the BODIPY dye family. Large two-photon absorption cross sections and long wavelength fluorescence emissions further enhance the competitiveness of Mem-SQAC as a membrane marker. By using Mem-SQAC, significant morphological changes of plasma membranes have been monitored during heavy metal poisoning and drug induced apoptosis of MCF-7 cells; the change tendencies are so distinctly different from each other that they can be used as indicators to distinguish different cell injuries. Further on, the complete processes of endocytosis toward Staphylococcus aureus and Escherichia coli by RAW 264.7 cells have been dynamically tracked. It is discovered that plasma membranes take quite different actions in response to the two bacteria, information unavailable in previous research reports.

# Fluorescent and Photostable Silicon Nanoparticles Sensors for Real-Time and Long-Term Intracellular pH Measurement in Live Cells\_2016

This paper describes the design and synthesis of a photostable, far-red to near-infrared (NIR) platform for optical voltage sensing. We developed a new, sulfonated silicon rhodamine fluorophore and integrated it with a phenylenevinylene molecular wire to create a Berkeley Red Sensor of Transmembrane potential, or BeRST 1 (“burst”). BeRST 1 is the first member of a class of far-red to NIR voltage sensitive dyes that make use of a photoinduced electron transfer (PeT) trigger for optical interrogation of membrane voltage. We show that BeRST 1 displays bright, membrane-localized fluorescence in living cells, high photostability, and excellent voltage sensitivity in neurons. Depolarization of the plasma membrane results in rapid fluorescence increases (24% ΔF/F per 100 mV). BeRST 1 can be used in conjunction with fluorescent stains for organelles, Ca2+ indicators, and voltage-sensitive fluorescent proteins. In addition, the red-shifted spectral profile of BeRST 1, relative to commonly employed optogenetic actuators like ChannelRhodopsin2 (ChR2), which require blue light, enables optical electrophysiology in neurons. The high speed, sensitivity, photostability and long-wavelength fluorescence profiles of BeRST 1 make it a useful platform for the noninvasive, optical dissection of neuronal activity.

# Photostable Bipolar Fluorescent Probe for Video Tracking Plasma Membranes Related Cellular Processes\_2014

We report the synthesis and site-specific incorporation in oligodeoxynucleotides (ODNs) of an emissive deoxyuridine analog electronically conjugated on its C5-position with a 3-methoxychromone moiety acting as a fluorophore. When incorporated in ODNs, this fluorescent deoxyuridine analog exhibits remarkable photostability and good quantum yields. This deoxyuridine analog also displays a mega-Stokes shift, which allows for its use as an efficient donor for FRET-based studies when paired with the yellow emissive indocarbocyanine Cy3 acceptor.

# A Photostable Silicon Rhodamine Platform for Optical Voltage Sensing\_2015

The synthesis and characterization of a novel two-photon-absorbing fluorene derivative, LT1, selective for the lysosomes of HCT 116 cancer cells, is reported. Linear and nonlinear photophysical and photochemical properties of the probe were investigated to evaluate the potential of the probe for two-photon fluorescence microscopy (2PFM) lysosomal imaging. The cytotoxicity of the probe was investigated to evaluate the potential of using this probe for live two-photon fluorescence biological imaging applications. Colocalization studies of the probe with commercial Lysotracker Red in HCT 116 cells demonstrated the specific localization of the probe in the lysosomes with an extremely high colocalization coefficient (0.96). A figure of merit was introduced to allow comparison between probes. LT1 has a number of properties that far exceed those of commercial lysotracker probes, including higher two-photon absorption cross sections, good fluorescence quantum yield, and, importantly, high photostability, all resulting in a superior figure of merit. 2PFM was used to demonstrate lysosomal tracking with LT1.

# Design and Development of a Two-Color Emissive FRET Pair Based on a Photostable Fluorescent Deoxyuridine Donor Presenting a Mega-Stokes Shift\_2016

Single-stranded oligonucleotides stabilize highly fluorescent Ag nanoclusters, with emission colors tunable via DNA sequence. We utilized DNA microarrays to optimize these scaffold sequences for creating nearly spectrally pure Ag nanocluster fluorophores that are highly photostable and exhibit great buffer stability. Five different nanocluster emitters have been created with tunable emission from the blue to the near-IR and excellent photophysical properties. Ensemble and single molecule fluorescence studies show that oligonucleotide encapsulated Ag nanoclusters exhibit significantly greater photostability and higher emission rates than commonly used cyanine dyes.

# High-Fidelity Hydrophilic Probe for Two-Photon Fluorescence Lysosomal Imaging\_2010

The present study demonstrates the near-field effect of silver nanostructure island films (SNIFs) on the photophysics and exited-state dynamics of quinine sulphate (QS) and its di-cation (QSD), doped in polyvinyl alcohol (PVA) films. The results indicate a nearly 3.8-fold enhancement in absorption and 4000-fold enhancement in fluorescence in SNIF-coated QS-doped PVA films, whereas only twofold enhancement in absorption and sevenfold enhancement in fluorescence intensity are found in SNIF-coated QSD-doped PVA films. However, an increase in photostability and a decrease in decay time have been observed in both the SNIF-coated films as compared to their uncoated forms. Further, a decrease in the magnitude of the edge excitation red shift in emission spectra along with a red shift in the La band and a rise in the intensity of the Lb band of excitation is observed in SNIF-coated QSD films because of strong coupling of the Lb band with the surface plasmons of silver nanoparticles. Moreover, X-ray photoelectron spectroscopic measurement of silver nanoparticle-coated QS–PVA films shows no change in 3d3/2 and 3d5/2 transitions of silver, whereas the decrease in energy in these silver transitions in the QSD–PVA system is observed as compared to silver nanoparticle-coated PVA films. These results indicate the formation of a field-governed radiating plasmon and plasmon-coupled unified fluorophore system, respectively. This affects the photophysics of both of the molecules by plasmonic coupling of the Frank–Condon state, solvent relaxation state, and charge-transfer state by different orders of magnitude.

# Oligonucleotide-Stabilized Ag Nanocluster Fluorophores\_2008

In this letter, we describe the preparation of a versatile polymer ligand, which can be attached to CdSe/ZnS semiconductor nanocrystals via a phase transfer reaction. The ligand is based on a chain of reactive esters, which can, in principle, be substituted by any compound containing amino-functionalities. The polymer/nanocrystal complexes are characterized in terms of structure and photostability.

# Excited-State Dynamics of Quinine Sulfate and Its Di-Cation Doped in Polyvinyl Alcohol Thin Films Near Silver Nanostructure Islands\_2019

The use of 157 nm as the next lower wavelength for photolithography for the production of semiconductors has created a need for transparent and radiation-durable polymers for use in soft pellicles, the polymer films which protect the chip from particle deposition. The most promising materials for pellicles are fluorinated polymers, but currently available fluorinated polymers undergo photodegradation and/or photodarkening upon long term exposure to 157 nm irradiation. To understand the mechanism of the photodegradation and photodarkening of fluorinated polymers, mechanistic studies on the photolysis of liquid model fluorocarbons, including perfluorobutylethyl ether and perfluoro-2H-3-oxa-heptane, were performed employing UV, NMR, FTIR, GC, and GC/MS analyses. All hydrogen-containing compounds showed decreased photostability compared to the fully perfluorinated compounds. Irradiation in the presence of atmospheric oxygen showed reduced photostability compared to deoxygenated samples. Photolysis of the samples was performed at 157, 172, 185, and 254 nm and showed only minor wavelength dependence. Mechanisms for photodegradation of the fluorocarbons are proposed, which involve Rydberg excited states. Time-dependent density functional theory has been used to predict the excitation spectra of model compounds.

# Semiconductor Nanocrystals with Multifunctional Polymer Ligands\_2002

4-Hydroxybenzothiazole (4-HBT) is a molecular constituent of pheomelanin—a polymeric skin centered pigment which acts as a natural photoprotector against harmful solar-UV radiation. Its molecular structure is therefore required to sustain a degree of photostability upon electronic excitation with UV irradiation. Despite its function as a protector against UV, pheomelanin is known to be less photostable than that of its close derivative eumelanin—a dark skin centered pigment. The 4-HBT subunit has long being attributed as a key contributor to the lack of photostability of pheomelanin—a hypothesis which we aim to test in this paper. Using high-level multireference computational methods, coupled with on-the-fly surface-hopping molecular dynamics, we find excited state reaction paths that show potential detriment to 4-HBT, leading to phototoxic radicals and products that are distinct from the original ground state molecule. Such radicals and photoproducts include those formed by classic πσ\* photodissociations, intramolecular proton-transfer, and ring-opening reactions. Such reactions shed light on the types of molecular structure that show photodetrimental effects upon UV irradiation, allowing judicious predictions for synthetic analogues that may offer enhanced photoprotection in commercial sunscreens.

# 157 nm Pellicles (Thin Films) for Photolithography:  Mechanistic Investigation of the VUV and UV-C Photolysis of Fluorocarbons\_2005

Correlated time-dependent density functional theory (TDDFT) quantum mechanical and pseudo-atomistic Monte Carlo (PAMC) statistical mechanical methods have been used to assist in the understanding of and to guide the improvement of organic electro-optic (OEO) materials, prepared by electric field poling of π-electron chromophore-containing materials near their glass transition temperature. Theoretical treatment of the effects of dielectric permittivity and optical frequency on molecular (chromophore) first hyperpolarizabilities has been carried out as well as the analysis of the influence of spatially anisotropic intermolecular electrostatic interactions on the poling-induced noncentrosymmetric order of chromophores. Three classes of OEO materials have been considered in correlated theoretical and experimental investigations: (1) traditional chromophore/polymer composite materials, (2) chromophores covalently incorporated into polymers, dendrimers, and dendronized polymers, and (3) recently discovered materials consisting of chromophores incorporated into chromophore-containing host materials. This latter class of materials is referred to as binary chromophore organic glasses (BCOGs). These BCOGs exhibit exceptional electro-optic activity because of a combination of high chromophore number density, the effect of high dielectric permittivity on molecular first hyperpolarizability, and improved acentric order arising from the intermolecular electrostatic interactions among the two types of chromophores. The electrical conductivity of materials can also influence achievable electro-optic activity, and thin metal oxide buffer layers, introduced to limit charge injection, can significantly improve poling efficiency. Chromophore order can also be influenced, in some cases, by novel processing techniques, such as laser-assisted electric field poling. Thermal and photostability are important parameters for practical application of materials and have been improved dramatically in recent times. Diels−Alder and fluorovinyl ether cycloaddition reactions have been used to elevate final material glass transition temperatures to above 200 °C. Photostability is dominated by the photoactivation of singlet oxygen and subsequent attack on electro-optic chromophores. Photostability can be improved by more than 4 orders of magnitude by chromophore modification and material packaging.

# Origins of Photodamage in Pheomelanin Constituents: Photochemistry of 4-Hydroxybenzothiazole\_2018

A ring-locked, phenyltetraene-based, second-order nonlinear optical chromophore (CLD-1) was synthesized. It shows no drop in decomposition temperature compared to its phenyltriene analogue, while the molecular nonlinearity increases by a factor of 2.25 from 6252 × 10-48 to 14065 × 10-48 esu at 1.9 μm. Thin films and waveguide devices were prepared from CLD-1/PMMA and CLD-1/APC (an amorphous polycarbonate) composites to study its electrooptic (EO) activity, optical loss, and photostability. An average EO coefficient of 92 pm/V at 1.06 μm was achieved in a 25 wt % CLD-1/APC composite. Mach−Zender (MZ) modulators fabricated from CLD-1/APC showed good thermal stability, low optical loss, low modulation voltage, and high extinction ratio. The photochemical stability of the CLD-1/APC modulator can be dramatically improved by operating in an inert gas atmosphere. Evidence shows that the predominant photochemical degradation mechanism of the material in air at 1.55 μm is the reaction between oxygen and photoexcited polyene-based chromophores.

# Theory-Inspired Development of Organic Electro-optic Materials\_2009

Cellular RNA dynamics are closely associated with a vast range of physiological processes that are mostly long-lasting. To uncover the association between RNA dynamics and these processes, fluorescent RNA probes with high specificity, photostability, and biocompatibility are compulsory. Herein, a series of fluorescent carbon dots (CDs) have been prepared by one-pot hydrothermal treatment of o-, m-, or p-phenylenediamines with triethylenetetramine. Only CDs derived from the meta precursor (m-CDs) with excellent photostability and biocompatibility can specifically bind to cellular RNA, allowing successfully long-term (up to 3 days) monitoring of RNA dynamics during cell apoptosis, mitosis, and proliferation. This RNA affinity can be attributed to the isoquinoline moieties and amines on the surface of m-CDs, which can bind to RNA through π–π stacking and electrostatic bonding, respectively. The cellular internalization of m-CDs is time-, temperature-, ATP-, caveolar, and microtubule-dependent. Additionally, investigations on the in vivo behavior of m-CD suggest that they can be efficiently and rapidly excreted from the zebrafish larvae body after 48 h. Our results provide a powerful tool for clarifying complex relationships between RNA dynamics and basic biological processes, disease development, or drug interactions.

# Low Vπ Electrooptic Modulators from CLD-1:  Chromophore Design and Synthesis, Material Processing, and Characterization\_2001

A Pd-catalyzed cascade reaction of four versatile privileged synthons is described. The sequential reaction involves the formation of five new chemical bonds by concatenating three distinct chemical steps. One of the derivatives exhibited absorption in the visible region, fluorescence with a high quantum yield, and excellent photostability. Its application is explored in live cell imaging, which exhibited cytoplasmic and mitochondrial specific staining with no toxicity.

# Dynamically Long-Term Imaging of Cellular RNA by Fluorescent Carbon Dots with Surface Isoquinoline Moieties and Amines\_2018

For most of the single-molecule fluorescence studies to date, biomolecules of interest are labeled with small organic dyes which suffer from their limited photostability evidenced by blinking and photobleaching. An enzymatic oxygen scavenging system of glucose oxidase and catalase is widely used to improve the dye photostability but with the unfavorable side effect of producing gluconic acid. It is known that accumulation of this byproduct in solution can lead to considerable acidification, but the uncertainty in its severity under experimentally relevant conditions has been a long-standing area of concern due to the lack of a suitable assay. In this paper we report a fluorescence-based analytical assay for quantitatively assessing the acidification of oxygen scavenging systems in situ. By using a ratiometric, dual-emission dye, SNARF-1, we observed the presence and, for the first time, measured the severity of solution acidification due to the oxygen scavenging system for a number of conditions relevant to single-molecule studies. On the basis of the quantitative analysis of the acidification profile under these conditions, practical guidelines for optimizing the oxygen scavenging system are provided. This in situ assay should be applicable to a large variety of future single-molecule fluorescence studies.

# Pd-Catalyzed Four-Component Sequential Reaction Delivers a Modular Fluorophore Platform for Cell Imaging\_2019

[g]-Face π-expanded coumarins are synthesized by employing the Scholl cyclization method. These new arene-annulated dipolar coumarins display interesting absorption and fluorescent properties. The large Stokes shifts, tuneable fluorescent quantum yields, and high photostability reveal promise in bioimaging application.

# Acidification of the Oxygen Scavenging System in Single-Molecule Fluorescence Studies: In Situ Sensing with a Ratiometric Dual-Emission Probe\_2010

A new type of a highly fluorescent sulforhodamine dye, 221SR, was designed and synthesized using 7-azabicylco[2.2.1]heptyl moieties as the electron donating auxochrome groups. Using the prototypical dye tetramethylsulforhodamine, TMSR, as a benchmark, we show this new dye has higher fluorescent quantum yields, Φ, (Φ = 0.95 vs Φ = 0.65 at 20 °C), emission efficiencies that are invariant in the 20→ 60 °C temperature range (Φ = 0.95 vs Φ = 0.38 at 60 °C), and fluorescence lifetimes that increase with a rise in temperature (20 → 60 °C) as compared to a decrease for the benchmark dye (3.8 → 3.9 vs 2.8 → 1.7 ns). Importantly, photostability studies found the azabicyclic rhodamine to be many times more stable than its tetramethyl analogue. To the best our knowledge this is the first report of the use of an apex-N-substituted azabicycloalkane as an electron donor group in any class of donor−acceptor dye. Thus, the concept of using an apex-substitutes bicyclic amine as a donor moiety constitutes a new paradigm for simultaneously inducing remarkable beneficial effects on both emission efficiency and photostability in a donor−acceptor fluorophore.

# Accessing [g]-Face π-Expanded Fluorescent Coumarins by Scholl Cyclization\_2019

Upconverting nanoparticles (UCNPs) have been studied as novel bioimaging probes owing to the absence of autofluorescence and excellent photostability. For practical applications, biocompatible UCNPs with high upconversion efficiency, bright luminescence, and good colloidal stability are desirable. Herein, we report a quantitative and systematic study on the upconversion luminescence from a set of NaYF4:Yb3+,Er3+-based nanoparticles by varying crystal structures, core/shell structures, and surface ligands. Upconversion luminescent properties in colloidal solution and at the single-particle level were examined. Hexagonal-phase core/shell UCNPs exhibited the most intense luminescence among various structures, while the excellent photostability was observed in all different types of UCNPs. To optimize the biomedical imaging capability of UCNPs, various surface coating strategies were tested. By quantitative spectroscopic measurements of surface-modified UCNPs in water, it was suggested that encapsulation with polyethylene glycol (PEG)-phospholipid was found to be effective in retaining both upconversion luminescence intensity and dispersibility in aqueous environment. Finally, UCNPs with different crystal structures were applied and compared in live cells.

# 7-Azabicyclo[2.2.1]heptane as a Unique and Effective Dialkylamino Auxochrome Moiety: Demonstration in a Fluorescent Rhodamine Dye\_2008

This is the first time the SnO2/PANI nanocomposite was utilized for the nitrogen oxide (NO) photocatalytic degradation. In addition, the properties of the SnO2/PANI nanocomposite were deeply studied by various characterizations. The results showed that the photostability of PANI has been improved and the SnO2/PANI nanocomposite demonstrated the efficient NO photocatalytic degradation. Notably, in this work, the adsorption and photocatalytic mechanisms, polymer photodegradation, and the band structure of the SnO2/PANI nanocomposite were fully and systematically investigated via experimental measurements and density functional theory (DFT).

# Comparative Study of Upconverting Nanoparticles with Various Crystal Structures, Core/Shell Structures, and Surface Characteristics\_2013

The importance of developing photoluminescent biodegradable scaffolding materials for tissue engineering is obvious, but it meets challenges with conventional biodegradable polymers such as aliphatic polyesters. In this study, photoluminescent biodegradable polyphosphazenes (PTA) were suggested as alternatives to target for long-term in vivo tracking applications. The PTA polymers were synthesized via nucleophilic cosubstitution of linear poly(dichlorophosphazene) with a fluorescent compound (TPCA) and alanine ethyl ester. The TPCA, with high fluorescent intensity and high quantum yield (∼0.5), was synthesized from citric acid and 2-aminoethanethiol. The resulted PTA polymers demonstrated adjustable degradation rates and fluorescent intensities in relating to their chemical compositions. In comparison with TPCA, the photostability of PTA polymers has been significantly improved, which made the long-term in vivo tracking feasible. PTA polymers were proven biocompatible and noncytotoxic for biomedical applications via both in vitro cell culture and in vivo implantation evaluations. During the 24-week subcutaneous implantation in mouse, the location and the degradation of PTA polymer were clearly visualized with the aid of fluorescent excitation and emission. In summary, PTA polymers were envisioned as good choices for tissue regeneration as scaffolding materials with in situ bioimaging potentials.

# Insight into the Photocatalytic Mechanism of Tin Dioxide/Polyaniline Nanocomposites for NO Degradation under Solar Light\_2018

Novel β-furan-fused bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (BOPHY) fluorescent dyes (F-BOPHY1–3) were prepared through an efficient process, and their structures were confirmed by 1H NMR spectroscopy, 13C NMR spectroscopy, MALDI-TOF HRMS, and element analysis. Their optical properties were then characterized by UV–vis absorption and photoluminescence (PL) spectroscopy. The UV–vis absorption and PL spectra of the dyes shifted to longer wavelengths relative to those of BOPHY because of the fusion of their furan rings, which extended π-conjugation of the molecules. All of the dyes exhibited large extinction coefficients (109700–12300 M–1 cm–1), deep-red fluorescence emission (646–667 nm), moderate fluorescence quantum yields (0.30–0.45), as well as high chemical stability and photostability in solution. These advantageous properties show that these compounds are important to the design of efficient long-wavelength fluorescent dyes and are suitable for various applications in biotechnology and materials science.

# Synthesis and Fluorescent Property of Biodegradable Polyphosphazene Targeting Long-Term in Vivo Tracking\_2016

Tin perovskite nanomaterial is one of the promising candidates to replace organic lead halide perovskites in lighting applications. Unfortunately, the performance of tin-based systems is markedly inferior to those featuring toxic Pb salts. In an effort to improve the emission quantum efficiency of nanoscale 2D layered tin iodide perovskites through fine-tuning the electronic property of organic ammonium salts, we came to unveil the relationship between dielectric confinement and the photoluminescent properties of tin iodide perovskite nanodisks. Our results show that increasing the dielectric contrast for organic versus inorganic layers leads to a bathochromic shift in emission peak wavelength, a decrease of exciton recombination time, and importantly a significant boost in the emission efficiency. Under optimized conditions, a leap in emission quantum yield to a record high 21% was accomplished for the nanoscale thienylethylammonium tin iodide perovskite (TEA2SnI4). The as-prepared TEA2SnI4 also possessed superior photostability, showing no sign of degradation under continuous irradiation (10 mW/cm2) over a period of 120 h.

# β-Furan-Fused bis(Difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine Fluorescent Dyes in the Visible Deep-Red Region\_2016

Hybrid two-dimensional (2D) lead halide perovskites have been employed in optoelectronic applications, including white-light emission for light-emitting diodes (LEDs). However, until now, there have been limited reports about white-light-emitting lead halide perovskites with experimental insights into the mechanism of the broadband emission. Here, we present white-light emission from a 2D hybrid lead chloride perovskite, using the widely known phenethylammonium cation. The single-crystal X-ray structural data, time-resolved photophysical measurements, and density functional theory calculations are consistent with broadband emission arising from strong exciton–phonon coupling with the organic lattice, which is independent of surface defects. The phenethylammonium lead chloride material exhibits a remarkably high color rendering index of 84, a CIE coordinate of (0.37,0.42), a CCT of 4426, and photostability, making it ideal for natural white LED applications.

# Harnessing Dielectric Confinement on Tin Perovskites to Achieve Emission Quantum Yield up to 21%\_2019

Literature reports detail the theory for strong electric-field enhancements sustained and localized on gold nanostars (NSs). The enhanced fields are expected to alter the fluorescence of nearby fluorophores. However, there are very few literature reports on experimental evidence for enhanced fluorescence from dyes bound to gold NSs. Furthermore, the literature lacks experimental studies on metal-enhanced fluorescence under near-infrared (NIR) two-photon excitation. In our work, a nanoassembly was made with a NS at the core, then coated with avidin followed by biotinylated-DNA-linkers that hybridized to different Cy3-labeled DNA strands. We will discuss experimental results on physical insights including: (1) how the nanoassembly synthesis conditions and dye orientation affected the fluorescence enhancement and (2) how the NSs affected the organic fluorophore’s photostability—both under NIR two-photon excitation. We observed enhancement factors ranging from 1.2 to 3.5 depending on the nanoassembly synthesis conditions. A biotin displacement experiment supported the fluorescence enhancement results. Our work contributes new knowledge and empirical insights that will enable advances in the field of colloidal dye NS-based applications.

# Morphology-Independent Stable White-Light Emission from Self-Assembled Two-Dimensional Perovskites Driven by Strong Exciton–Phonon Coupling to the Organic Framework\_2017

Polydopamine-capped cobalt phosphide nanorods (Co2P@PDA NRs) with six aspect ratios (ARs) from 1.4 to 10 are synthesized by a one-step thermal decomposition and microemulsion method. The NRs with AR ∼ 6.4 show good dispersibility in physiological solutions, exhibiting an outstanding near-infrared (NIR) photothermal performance because of a high molar extinction coefficient of 13.08 L g–1 cm–1 at 980 nm, excellent photostability, a photothermal conversion efficiency (PCE) of ∼64%, and no obvious cytotoxicity to various types of cells. Coupled with NIR excitation, folic acid conjugation to the doxorubicin-loaded NRs (AR ∼ 6.4) helped them in securing targeted and controlled drug release to the cancer cells. The synergistic photochemothermal property of Co2P@PDA NRs offers itself as a worthy candidate in tumor theranostic applications.

# Lighting up Plasmonic Nanostar Colloids for Metal-Enhanced Fluorescence under Two-Photon Near-Infrared Excitation\_2018

We herein introduce a facile, low-cost photochemical method capable of rapid (<40 min) and large-quantity (∼10 g) production of highly fluorescent (quantum yield: 25%) silicon nanoparticles (SiNPs) of tunable optical properties (peak emission wavelength in the range of 470–560 nm) under ambient air conditions, by introducing 1,8-naphthalimide as a reducing agent and surface ligands. The as-prepared SiNPs feature robust storage stability and photostability preserving strong and stable fluorescent during long-term (>3 h) high-power UV irradiation, in contrast to the rapid fluorescence quenching within 2 h of conventional organic dyes and II–VI quantum dots under the same conditions. The as-prepared SiNPs serving as photostable nanoprobes are workable for cellular imaging in long-term manners. Our findings provide a powerful method for mild-condition and low-cost, large-quantity production of highly fluorescent and photostable SiNPs for various promising applications.

# Cobalt Phosphide Nanorods with Controlled Aspect Ratios as Synergistic Photothermo-Chemotherapeutic Agents\_2018

Ferric ion (Fe3+) plays a vital role in cellular homeostasis. However, the detection of Fe3+ with rhodamine B (RhB) has potential problems, such as poor selectivity and low photostability. To address these problems, we rationally designed an RhB@MOF nanocomposite-based “on–off–on” fluorescent switching nanoprobe for highly sensitive and selective detection of Fe3+ and ascorbic acid. This RhB@MOF nanoprobe was prepared through a facile one-pot synthesis. Here MOF served as a selectivity regulator for the detection of Fe3+. By embedding RhB into the porous crystalline MOF, enhanced photostability and fluorescence lifetime of RhB to Fe3+ were achieved. The as-prepared RhB@MOF was demonstrated to be an ultrasensitive and selective nanoprobe for the detection of Fe3+ in human serum and ascorbic acid in rat brain microdialysate. Furthermore, inner filter effect (IFE) and photoinduced electron transfer (PET) were proposed and discussed to explain the selectivity and sensitivity of RhB to Fe3+ against other interfering substances. Our novel “on–off–on” nanoprobe provides insight into the rational design of MOF-based biosensors for selective and sensitive detection of analytes.

# Facile, Large-Quantity Synthesis of Stable, Tunable-Color Silicon Nanoparticles and Their Application for Long-Term Cellular Imaging\_2015

A new class of oxygen indicators is described. Platinum(II) and palladium(II) complexes of azatetrabenzoporphyrins occupy an intermediate position between tetrabenzoporphyrins and phthalocyanines and combine features of both. The new dyes are excitable in the red part of the spectrum and possess strong room-temperature NIR phosphorescence. Other features include excellent spectral compatibility with the red laser diodes and 632.8 nm line of He−Ne laser, excellent photostability, and significantly shorter decay times than for the respective meso-tetraphenyltetrabenzoporphyrins. Applicability of the complexes for optical oxygen sensing is demonstrated.

# A Metal–Organic Framework as Selectivity Regulator for Fe3+ and Ascorbic Acid Detection\_2019

Epicocconone is a natural latent fluorophore that is widely used in biotechnology because of its large Stokes shift and lack of fluorescence in its unconjugated state. However, the low photostability and quantum yields of epicocconone have limited its wider use, and in the absence of a total synthesis, this limitation has been a long-standing problem. Here we report a general strategy for the synthesis of epicocconone analogues that relies on a 2-iodoxybenzoic acid-mediated dearomatization and on the replacement of the triene tail of the natural product by an aromatic ring. This design element is general and the synthesis is straightforward, providing ready access to libraries of polyfunctional fluorophores with long Stokes shifts based on the epicocconone core. Our structural modifications resulted in analogues with increased photostability and quantum yields compared with the natural product. Staining proteomic gels with these new analogues showed significant lowering of the detection limit and a 30% increase in the number of low-abundance proteins detected. These epiccoconone analogues will substantially improve the discovery rate of biomarker needles in the proteomic haystack.

# Phosphorescent Platinum(II) and Palladium(II) Complexes with Azatetrabenzoporphyrins—New Red Laser Diode-Compatible Indicators for Optical Oxygen Sensing\_2010

Nanoscale metal–organic frameworks (NMOFs) have been applied for biomedical sensing in recent years. However, it is still a great challenge to construct a highly efficient NMOFs fluorescent probe for sensing in a biological system, with high signal-to-noise ratio, photostability, and deep tissue penetration. Herein, for the first time, we report the two-photon metal–organic framework (TP-MOF) as a sensing platform. The design of TP-MOF is based on NMOFs incorporating a target-responsive two-photon organic moiety through click chemistry. PCN-58, as a model building block, was covalently modified with a small-molecule probe for H2S or Zn2+ as model analytes. TP-MOF probes retain the fluorescence-responsive properties of the TP organic moiety and possess excellent photostability and selectivity, as well as biocompatibility. Benefiting from the near-infrared (∼820 nm) excited two-photon fluorophore, TP-MOF probes serve to sense and image their respective targets in live cells and tissue slices with a penetration of 130 μm. The molecular design presented here bodes well for the extension to other MOFs displaying sensing components for other analytes of interest.

# Design and Synthesis of Epicocconone Analogues with Improved Fluorescence Properties\_2014

Near-infrared (NIR) fluorescent probes are increasingly popular in biological imaging and sensing, as long-wavelength (650–900 nm) excitation and emission have the advantages of minimum photodamage, deep tissue penetration, and minimum interference from autofluorescence in living systems. Here, a series of long-wavelength BODIPY dyes SPC, DC-SPC, DPC, and DC-DPC are synthesized conveniently and efficiently. They exhibit excellent photophysical properties in far red to near-infrared region, including large extinction coefficients, high fluorescence quantum yields, good photostability, and reasonable two-photon absorption cross section. Comparison of single-molecular imaging confirms that DPC is a much more efficient and more photostable NIR fluorophore than the commonly used Cy5. Also importantly, two kinds of convenient functionalization sites have been reserved: the aryl iodide for organometallic couplings and the terminal alkyne groups for click reactions. Further derivatives DC-SPC-PPh3 exhibit specificity to localize in mitochondria. The introduction of triphenylphosphonium (TPP) moieties mediates its hydrophilic–lipophilic balance and makes DC-SPC-PPh3 appropriate for cell labeling. Their long-wavelength emission at ∼650 nm can efficiently avoid the spectral crosstalk with other probes emitting in the visible light region. Superior photostability, low cytotoxicity, and two-photon excitable properties demonstrate its utility as a standard colocalizing agent to estimate the other probes’ local distribution.

# Nanoscale Metal–Organic Framework Based Two-Photon Sensing Platform for Bioimaging in Live Tissue\_2019

Bright two-photon fluorescent probes are highly desirable to be able to optically probe biological activities deep inside living organisms with larger imaging depth, minor autofluorescence background, and less photodamage. In this study, we report the biocompatible nitrogen-doped graphene quantum dots (N-GQDs) as efficient two-photon fluorescent probes for cellular and deep-tissue imaging. The N-GQD was prepared by a facile solvothermal method using dimethylformamide as a solvent and nitrogen source. The two-photon absorption cross-section of N-GQD reaches 48 000 Göppert-Mayer units, which far surpasses that of the organic dyes and is comparable to that of the high performance semiconductor QDs, achieving the highest value ever reported for carbon-based nanomaterials. More importantly, a study of penetration depth in tissue phantom demonstrates that the N-GQD can achieve a large imaging depth of 1800 μm, significantly extending the fundamental two-photon imaging depth limit. In addition, the N-GQD is nontoxic to living cells and exhibits super photostability under repeated laser irradiation. The high two-photon absorption cross-section, large imaging depth, good biocompatibility, and extraordinary photostability render the N-GQD an attractive alternative probe for efficient two-photon imaging in biological and biomedical applications.

# Long-Wavelength, Photostable, Two-Photon Excitable BODIPY Fluorophores Readily Modifiable for Molecular Probes\_2013

In this article, near-infrared (NIR) CdHgTe alloyed quantum dots (QDs) were directly synthesized in water by heating a mixed solution of CdCl2, Hg(ClO4)2 and NaHTe in the presence of thiol stabilizers. The CdHgTe QDs exhibit photoluminescence (PL) ranging from 600 to 830 nm that can be tuned by size and composition. The quantum yields (QYs) of QDs were about 20−50%, associated with their emission wavelength and composition. Compared to other reported NIR QDs such as CdTe/CdHgTe and InAs, the as-prepared CdHgTe alloyed QDs have much narrower emission spectra, and their full widths at half-maximum (fwhm) are only 60−80 nm. Characterization by HRTEM and XRD showed that the CdHgTe QDs have good monodispersity and a nice crystal structure. To improve the photostability and reduce the cytotoxity of the CdHgTe QDs, a CdS nanocrystal shell was added to the surface of the CdHgTe QD core. Furthermore, the CdHgTe/CdS core/shell QDs were successfully applied for the imaging of living animals. Our preliminary results illustrate that our synthesis procedure is very simple and inexpensive and that the as-prepared products CdHgTe/CdS core/shell QDs are water-soluble and photostable and will be an alternative probe in the imaging of living animals.

# Strong Two-Photon-Induced Fluorescence from Photostable, Biocompatible Nitrogen-Doped Graphene Quantum Dots for Cellular and Deep-Tissue Imaging\_2013

We describe a poly(methyl methacrylate) (PMMA) dip-coating procedure, which results in surface stabilization of phosphonate and carboxylate derivatives of Ru(II)-polypyridyl complexes surface-bound to mesoporous nanoparticle TiO2 and nanoITO films in aqueous solutions. As shown by contact angle and transmission electron microscopy (TEM) measurements, PMMA oligomers conformally coat the metal-oxide nanoparticles changing the mesoporous films from hydrophilic to hydrophobic. The thickness of the PMMA overlayer on TiO2–Ru(II) can be controlled by changing the wt % of PMMA in the dipcoating solution. There are insignificant perturbations in electrochemical or spectral properties at thicknesses of up to 2.1 nm with the Ru(III/II) couple remaining electrochemically reversible and E1/2 values and current densities nearly unaffected. Surface binding by PMMA overlayers results in stable surface binding even at pH 12 with up to a ∼100-fold enhancement in photostability. As shown by transient absorption measurements, the MLCT excited state(s) of phosphonate derivatized [Ru(bpy)2((4,4′-(OH)2PO)2bpy)]2+ undergo efficient injection and back electron transfer with pH independent kinetics characteristic of the local pH in the initial loading solution.

# High-Quality and Water-Soluble Near-Infrared Photoluminescent CdHgTe/CdS Quantum Dots Prepared by Adjusting Size and Composition\_2007

One-dimensional nanomaterials have attracted great interest in both fundamental research and technological applications because they can function as device elements and be used to effectively generate, guide, and detect light. Here we report a gold nanorod-enhanced light emission in quantum-dot-doped polymer nanofibers. By incorporating gold nanorods into quantum-dot-doped polymer nanofiber, a 67% increment in 600 nm red light emission efficiency was obtained with an extinction coefficient of 100 cm–1, a low excitation power operation of 100 nW, and a 100 min increment in photostability.

# Stabilization of Ruthenium(II) Polypyridyl Chromophores on Nanoparticle Metal-Oxide Electrodes in Water by Hydrophobic PMMA Overlayers\_2014

Solar water splitting is an alternative way of clean and sustainable hydrogen production. Tantalum nitride (Ta3N5) is one of the promising candidates that recently attracted a great amount of attention as photoelectrodes for solar water splitting. Nevertheless, it suffers severely from photocorrosion in an aqueous solution. Therefore, the precise selection of a cocatalyst, in terms of the material, the amount, and the way of its deposition, is indispensable to highly improve its water splitting performance. In the present work, we introduce a Fe–Ni–Co mixed-metal oxide as a water oxidation cocatalyst that remarkably improved the photocurrent and photostability of the pristine Ta3N5 photoanode. The cocatalyst-modified electrode showed a photocurrent of about 4.0 mA cm–2 at 1.23 V vs RHE in 1 M NaOH. The electrode maintained 100% and 96% of the initial photocurrent after irradiation times of 1 and 2 h, respectively. In addition, a continuous evolution of hydrogen and oxygen occurred for 2 h at quantitative Faraday efficiencies (>96%). This photostability is superior compared to that of the other single-layer modified Ta3N5 photoanodes reported so far. It is noteworthy that the anodic spark deposition is used to fabricate precursor electrodes (NaTaO3), which then were converted to Ta3N5 by nitridation in an ammonia atmosphere.

# Gold Nanorod-Enhanced Light Emission in Quantum-Dot-Doped Polymer Nanofibers\_2014

This paper reports a novel method to tune the fluorescence properties of fluorescein (FLU) in a 2D matrix of layered double hydroxide (LDH) by changing the interlayer microenvironment. FLU and surfactants with different alkyl chain lengths were cointercalated in the galleries of a Zn2Al LDH by the anion exchange method. Thin films of FLU-CnH2n+1SO3/LDH (n = 5, 6, 7, 10, and 12, respectively; n stands for the number of carbon in the alkyl chain), which possess a well c-orientation revealed by XRD and SEM, were obtained by the solvent evaporation method on Si substrates. It was found that the orientation of FLU and its anisotropy, fluorescence wavelength, fluorescence quantum yield, and lifetime correlate with the microenvironment of the LDH gallery, which can be tuned by simply changing the alkyl chain length of the surfactant. The optimal fluorescence quantum yield, anisotropy, the longest fluorescence lifetime and the strongest photostability of the FLU-CnH2n+1SO3/LDH film can be obtained with n = 7, due to the “size-matching” rule between the organic dye and surfactant.

# Enhanced Performance of Pristine Ta3N5 Photoanodes for Solar Water Splitting by Modification with Fe–Ni–Co Mixed-Metal Oxide Cocatalysts\_2017

Carbon materials are excellent candidates for photovoltaic solar cells: they are Earth-abundant, possess high optical absorption, and maintain superior thermal and photostability. Here we report on solar cells with active layers made solely of carbon nanomaterials that present the same advantages of conjugated polymer-based solar cells, namely, solution processable, potentially flexible, and chemically tunable, but with increased photostability and the possibility to revert photodegradation. The device active layer composition is optimized using ab initio density functional theory calculations to predict type-II band alignment and Schottky barrier formation. The best device fabricated is composed of PC70BM fullerene, semiconducting single-walled carbon nanotubes, and reduced graphene oxide. This active-layer composition achieves a power conversion efficiency of 1.3%—a record for solar cells based on carbon as the active material—and we calculate efficiency limits of up to 13% for the devices fabricated in this work, comparable to those predicted for polymer solar cells employing PCBM as the acceptor. There is great promise for improving carbon-based solar cells considering the novelty of this type of device, the high photostability, and the availability of a large number of carbon materials with yet untapped potential for photovoltaics. Our results indicate a new strategy for efficient carbon-based, solution-processable, thin film, photostable solar cells.

# Tunable Photoluminescence Properties of Fluorescein in a Layered Double Hydroxide Matrix by Changing the Interlayer Microenvironment\_2010

Ab initio molecular dynamics including nonadiabatic and spin–orbit couplings on equal footing is used to unravel the deactivation of cytosine after UV light absorption. Intersystem crossing (ISC) is found to compete directly with internal conversion in tens of femtoseconds, thus making cytosine the organic compound with the fastest triplet population calculated so far. It is found that close degeneracy between singlet and triplet states can more than compensate for very small spin–orbit couplings, leading to efficient ISC. The femtosecond nature of the ISC process highlights its importance in photochemistry and challenges the conventional view that large singlet–triplet couplings are required for an efficient population flow into triplet states. These findings are important to understand DNA photostability and the photochemistry and dynamics of organic molecules in general.

# Nanocarbon-Based Photovoltaics\_2012

Progress in fluorescence detection and imaging technologies depends on the availability of fluorescent labels with strong light absorption/emission characteristics. We have synthesized intercalator dye arrays on a compact 3-dimensional DNA-tetrahedron nanostructure. The template tolerates the structural distortions introduced by intercalation and allows concentration of multiple fluorophores within a small volume, resulting in brightly fluorescent nanotags with effective extinction coefficients in the order of 106 M−1 cm−1. Efficient energy transfer from intercalated donor dyes to covalently attached acceptor dyes in the nanotags allows the emission wavelength to be shifted to the red relative to the excitation light, providing wavelength tunability. The compact nature of the supramolecular DNA tetrahedron also provides a protective medium for the fluorophores, leading to improved photostability and enhanced resistance to nuclease digestion, relative to one- or two-dimensional nanotags described previously.

# Femtosecond Intersystem Crossing in the DNA Nucleobase Cytosine\_2012

As the feet of clay, photocorrosion induced by hole accumulation has placed serious limitations on the widespread deployment of sulfide nanostructures for photoelectrochemical (PEC) water splitting. Developing sufficiently stable electrodes to construct durable PEC systems is therefore the key to the realization of solar hydrogen production. Here, an innovative charge-transfer manipulation concept based on the aligned hole transport across the interface has been realized to enhance the photostability of In2S3 electrodes toward PEC solar hydrogen production. The concept was realized by conducting compact deposition of In2S3 nanocrystals on the TiO2 nanowire array. Under PEC operation, the supporting TiO2 nanowires functioned as an anisotropic charge-transfer backbone to arouse aligned charge transport across the TiO2–In2S3 interface. Because of the aligned hole transport, the TiO2 nanowire-supported In2S3 hybrid nanostructures (TiO2–In2S3) exhibited improved hole-transfer dynamics at the TiO2–In2S3 interface and enhanced hole injection kinetics at the electrode surface, substantially increasing the long-term photostability toward solar hydrogen production. The PEC durability tests showed that TiO2–In2S3 electrodes can achieve nearly 90.9% retention of initial photocurrent upon continuous irradiation for 6 h, whereas the pure In2S3 merely retained 20.8% of initial photocurrent. This double-gain charge-transfer manipulation concept is expected to convey a viable approach to the intelligent design of highly efficient and sufficiently stable sulfide photocatalysts for sustainable solar fuel generation.

# Fluorescent DNA Nanotags Based on a Self-Assembled DNA Tetrahedron\_2009

Effective interface engineering has been shown to play a vital role in facilitating efficient charge-carrier transport, thus boosting the performance of organic photovoltaic devices. Herein, we employ water-soluble lacunary polyoxometalates (POMs) as multifunctional interlayers between the titanium dioxide (TiO2) electron extraction/transport layer and the organic photoactive film to simultaneously enhance the efficiency, lifetime, and photostability of polymer solar cells (PSCs). A significant reduction in the work function (WF) of TiO2 upon POM utilization was observed, with the magnitude being controlled by the negative charge of the anion and the selection of the addenda atom (W or Mo). By inserting a POM interlayer with ∼10 nm thickness into the device structure, a significant improvement in the power conversion efficiency was obtained; the optimized POM-modified poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2- 33 ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]:[6,6]-phenyl-C70 butyric acid methyl ester (PTB7:PC70BM)-based PSCs exhibited an efficiency of 8.07%, which represents a 21% efficiency enhancement compared to the reference TiO2 cell. Similar results were obtained in POM-modified devices based on poly(3-hexylthiophene) (P3HT) with electron acceptors of different energy levels, such as PC70BM or indene-C60 bisadduct (IC60BA), which enhanced their efficiency up to 4.34 and 6.21%, respectively, when using POM interlayers; this represents a 25–33% improvement as compared to the reference cells. Moreover, increased lifetime under ambient air and improved photostability under constant illumination were observed in POM-modified devices. Detailed analysis shows that the improvements in efficiency and stability synergistically stem from the reduced work function of TiO2 upon POM coverage, the improved nanomorphology of the photoactive blend, the reduced interfacial recombination losses, the superior electron transfer, and the more effective exciton dissociation at the photoactive layer/POM/TiO2 interfaces.

# Low Work Function Lacunary Polyoxometalates as Electron Transport Interlayers for Inverted Polymer Solar Cells of Improved Efficiency and Stability\_2017

Nucleoli are important subnuclear structures inside cells. We report novel fluorescent gold nanoclusters (K–AuNCs) that are able to stain the nucleoli selectively and make it possible to explore the nucleolar morphology with fluorescence imaging technique. This novel probe is prepared through an easy synthesis method by employing a tripeptide (Lys–Cys–Lys) as the surface ligand. The properties, including deep-red fluorescence emission (680 nm), large Stocks shift, broad excitation band, low cytotoxicity, and good photostability, endow this probe with potential for bioanalytical applications. Because of their small size and their positively charged surface, K–AuNCs are able to accumulate efficiently at the nucleolar regions and provide precise morphological information. K–AuNCs are also used to monitor the nucleolar dynamics along the reverse-transformation process of malignant cells, induced by the agonist of protein A, 8-chloro-cyclic adenosine monophosphate. This gives a novel approach for investigating the working mechanism of antitumor drugs.

# TiO2 Nanowire-Supported Sulfide Hybrid Photocatalysts for Durable Solar Hydrogen Production\_2018

A new type of fluorescence sensory material with high sensitivity, selectivity, and photostability has been developed for vapor probing of organic amines. The sensory material is primarily based on well-defined nanofibers fabricated from an n-type organic semiconductor molecule, N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide. Upon deposition onto a substrate, the entangled nanofibers form a meshlike, highly porous film, which enables expedient diffusion of gaseous analyte molecules within the film matrix, leading to milliseconds response for the vapor sensing.

# Deep-Red Fluorescent Gold Nanoclusters for Nucleoli Staining: Real-Time Monitoring of the Nucleolar Dynamics in Reverse Transformation of Malignant Cells\_2017

Mitochondria trafficking plays an essential role for supplying energy in the neuronal system. We report here a red emissive two-photon probe for mitochondria (CMT-red) that showed high selectivity and robust staining ability for mitochondria, high photostability under a two-photon microscopy imaging condition, and low cytotoxicity. This probe can be easily loaded into live cells and tissue and used for real-time, high resolution imaging of the mitochondria trafficking in primary cortical neurons as well as in rat hippocampal tissue.

# Expedient Vapor Probing of Organic Amines Using Fluorescent Nanofibers Fabricated from an n-Type Organic Semiconductor\_2008

Fluorescently labeled starch nanocrystal (FL-SNC) was synthesized using a simple, low-cost, and scalable two-step chemical modification process. Reactive amino groups were introduced onto the SNC surface through silanization with 3-aminopropyl triethoxysilane (APTES), and fluorescein isothiocyanate (FITC) groups were covalently attached through thiourea. Fourier transform infrared spectrometry, X-ray photoelectron spectroscopy, solid-state cross-polarization magic-angle spinning 13C NMR, UV–visible absorbance spectrophotometry, and fluorescence emission spectroscopy confirmed the successful introduction of the fluorescent groups. Transmission electron microscopy and X-ray diffraction data indicated that the dispersibility of FL-SNC was significantly improved, and the original crystallinity and morphology were retained. Compared with a mixture of uncoupled FITC and SNC, covalently connected FL-SNC displayed a more obvious fluorescence intensity and higher photostability. Furthermore, FL-SNC was biocompatible with cells and could be easily internalized. In combination with the participation of active hydroxyls, this facile approach has potential use for synthesis of fluorescently polyhydroxyl nanoparticles and can be widely used for making biosensors and biomarker in food and biomedical industries.

# Red Emissive Two-Photon Probe for Real-Time Imaging of Mitochondria Trafficking\_2014

We report on the fluorescence properties and the combined effects of energy diffusion and energy transfer in polyfluorene nanoparticles doped with a variety of fluorescent dyes. As the doping host, polyfluorene possesses extraordinary “light harvesting” ability, resulting in higher per-particle brightness as compared to dye-loaded silica nanoparticles of similar dimensions. Both the steady-state fluorescence spectra and time-resolved fluorescence measurements indicate highly efficient energy transfer from the host polymer to the acceptor dye molecules. A model that takes into account the combined effects of energy diffusion, Förster transfer, and particle size was developed. Comparisons of experimental data to the model results elucidate the importance of particle size and energy diffusion within the polymer in determining the optical properties of the doped conjugated polymer nanoparticles. Fluorescence quantum yields of ∼40% and peak extinction coefficients of 1.5 × 109 M-1cm-1 were determined for aqueous suspensions of ∼30 nm diameter polymer nanoparticles doped with perylene or coumarin 6 (2 wt %). Photobleaching experiments indicate that energy transfer phenomena strongly influence the photostability of these dye-doped nanoparticles. Significant features of these nanoparticles include the high brightness, highly red-shifted emission spectrum, and excellent photostability, which are promising for biological labeling and sensing applications. In addition, the nanoparticles are a useful model system for studying energy transfer in dense, nanostructured, multichromophoric systems.

# Facile Method for Fluorescent Labeling of Starch Nanocrystal\_2017

Intracellular pH (pHi) plays a critical role in the physiological and pathophysiological processes of cells, and fluorescence imaging using pH-sensitive indicators provides a powerful tool to assess the pHi of intact cells and subcellular compartments. Here we describe a nanoparticle-based ratiometric pH sensor, comprising a bright and photostable semiconductor quantum dot (QD) and pH-sensitive fluorescent proteins (FPs), exhibiting dramatically improved sensitivity and photostability compared to BCECF, the most widely used fluorescent dye for pH imaging. We found that Förster resonance energy transfer between the QD and multiple FPs modulates the FP/QD emission ratio, exhibiting a >12-fold change between pH 6 and 8. The modularity of the probe enables customization to specific biological applications through genetic engineering of the FPs, as illustrated by the altered pH range of the probe through mutagenesis of the fluorescent protein. The QD-FP probes facilitate visualization of the acidification of endosomes in living cells following polyarginine-mediated uptake. These probes have the potential to enjoy a wide range of intracellular pH imaging applications that may not be feasible with fluorescent proteins or organic fluorophores alone.

# Energy Transfer in a Nanoscale Multichromophoric System:  Fluorescent Dye-Doped Conjugated Polymer Nanoparticles\_2008

A facile and simple one-step method was developed to fabricate aptamer-decorated self-assembled organic dots with aggregation-induced emission (AIE) characteristics. With integration of the advantages of AIE aggregates with strong emission and the cell-targeting capability of aptamers, the as-prepared Apt-AIE organic nanodots can specifically target to cancer cells with good biocompatibility, high image constrast, and photostability. On the basis of this universal method, a variety of versatile organic fluorescent nanoprobes with high brightness, specific recognition, and clinical-transitional potential could be facilely constructed for biological sensing and imaging applications.

# Quantum Dot–Fluorescent Protein FRET Probes for Sensing Intracellular pH\_2012

We examined the effects of silver island films on multiphoton excitation of rhodamine derivatives and biochemical fluorophores. The fluorophores were studied in approximately 1 μm thick samples between two quartz slides coated with silver islands. Intensity and lifetime measurements of rhodamine B demonstrated enhanced two-photon excitation near the metal particles. Time-resolved measurements showed a decreased lifetime of RhB with two-photon excitation as compared to unsilvered quartz slides, which indicates the two-photon excitation was localized near the metal particles. Additionally, rhodamine B showed increased photostability with two-photon excitation near metal particles, which is consistent with the shorter lifetime. For lower quantum yield fluorophores such as rose bengal, eosin, 1-anilinonaphthalene-8-sulfonic acid, and coumarin 152, we found the emission from the micron thick sample was almost completely due to the fluorophores near the silver particles, perhaps to within 300 Å of the metal surfaces. These results suggest the use of metal particles for localized multiphoton excitation of biological macromolecules or cells. Additionally, one can imagine metal colloids with bound fluorophores being selectively excited when placed in highly fluorescent samples such as tissue samples.

# Aptamer-Decorated Self-Assembled Aggregation-Induced Emission Organic Dots for Cancer Cell Targeting and Imaging\_2017

Near-infrared plasmonic nanoparticles demonstrate great potential in disease theranostic applications. Herein a nanoplatform, composed of mesoporous silica-coated gold nanorods (AuNRs), is tailor-designed to optimize the photodynamic therapy (PDT) for tumor based on the plasmonic effect. The surface plasmon resonance of AuNRs was fine-tuned to overlap with the exciton absorption of indocyanine green (ICG), a near-infrared photodynamic dye with poor photostability and low quantum yield. Such overlap greatly increases the singlet oxygen yield of incorporated ICG by maximizing the local field enhancement, and protecting the ICG molecules against photodegradation by virtue of the high absorption cross section of the AuNRs. The silica shell strongly increased ICG payload with the additional benefit of enhancing ICG photostability by facilitating the formation of ICG aggregates. As-fabricated AuNR@SiO2–ICG nanoplatform enables trimodal imaging, near-infrared fluorescence from ICG, and two-photon luminescence/photoacoustic tomography from the AuNRs. The integrated strategy significantly improved photodynamic destruction of breast tumor cells and inhibited the growth of orthotopic breast tumors in mice, with mild laser irradiation, through a synergistic effect of PDT and photothermal therapy. Our study highlights the effect of local field enhancement in PDT and demonstrates the importance of systematic design of nanoplatform to greatly enhancing the antitumor efficacy.

# Multiphoton Excitation of Fluorescence near Metallic Particles:  Enhanced and Localized Excitation\_2002

Photoactivatable organic fluorophores and fluorescent proteins have been widely adopted for cellular imaging and have been critical for increasing temporal and spatial resolution, as well as for the development of superresolution microscopy techniques. At the same time, semiconducting nanocrystal quantum dots (QDs) have shown superior brightness and photostability compared to both organic fluorophores and proteins. As part of our efforts to develop nanoparticles with novel optical properties, we have synthesized caged quantum dots, which are nonluminescent under typical microscopic illumination but can be activated with stronger pulses of UV light. We show that ortho-nitrobenzyl groups efficiently quench QDs of different compositions and emissions and can be released from the nanoparticle surface with UV light, both in solution and in live cells. This caging is dependent on the emission of the QD, but it is effective through the visible spectrum into the nIR, offering a large array of new colors for photoactivatable probes. Like organic and protein-based photoactivatable probes, caged QDs can confer increased spatial and temporal resolution, with the added brightness and photostability of QDs.

# Localized Electric Field of Plasmonic Nanoplatform Enhanced Photodynamic Tumor Therapy\_2014

Porphyrin-based GUMBOS and nanoGUMBOS were synthesized for potential application as improved photosensitizing materials. In this study, porphyrin dyes [meso-tetra(4-carboxyphenyl)porphine (TCPP) and zinc(II) meso-tetra(4-carboxyphenyl)porphine (Zn-TCPP)] were selected as anions, and trihexyltetradecylphosphonium (P66614) was employed as a cation. The resulting [P66614]4[TCPP] and [P66614]4[Zn-TCPP] GUMBOS (group of uniform materials based on organic salts) provided high photostability and excellent thermal stability for these compounds. NanoGUMBOS, i.e., nanomaterials derived from GUMBOS, were synthesized using reprecipitation and ion association methods. The surface charges of these nanoparticles were tuned from positive to negative through use of an ion association synthetic method without the need for additives or stabilizers. When compared to the parent dyes, nanoGUMBOS exhibited excellent photodynamic properties for potential applications as photosensitizers. Evaluation of the electrochemical properties of these GUMBOS suggest that these compounds can be applied as photosensitizers in optoelectronic devices such as dye-sensitized solar cells.

# Caged Quantum Dots\_2008

High-efficiency colloidal quantum dot (CQD) solar cells (CQDSCs) with improved air stability were developed by employing potassium-modified ZnO as an electron-accepting layer (EAL). The effective potassium modification was achievable by a simple treatment with a KOH solution of pristine ZnO films prepared by a low-temperature solution process. The resulting K-doped ZnO (ZnO-K) exhibited EAL properties superior to those of a pristine ZnO-EAL. The Fermi energy level of ZnO was upshifted, which increased the internal electric field and amplified the depletion region (i.e., charge drift) of the devices. The surface defects of ZnO were effectively passivated by K modification, which considerably suppressed interfacial charge recombination. The CQDSC based on ZnO-K achieved improved power conversion efficiency (PCE) of ≈10.75% (VOC of 0.67 V, JSC of 23.89 mA cm–2, and fill factor of 0.68), whereas the CQDSC based on pristine ZnO showed PCE of 9.97%. Moreover, the suppressed surface defects of ZnO-K substantially improved long-term stability under air. The device using ZnO-K exhibited superior long-term air storage stability (96% retention after 90 days) compared to that using pristine ZnO (88% retention after 90 days). The ZnO-K-based device also exhibited improved photostability under air. Under continuous light illumination for 600 min, the ZnO-K-based device retained 96% of its initial PCE, whereas the pristine ZnO-based device retained only 67%.

# Synthesis and Characterization of Porphyrin-Based GUMBOS and NanoGUMBOS as Improved Photosensitizers\_2016

In recent years, photodynamic therapy (PDT) has drawn much attention as a noninvasive and safe cancer therapy method due to its fine controllability, good selectivity, low systemic toxicity, and minimal drug resistance in contrast to the conventional methods (for example, chemotherapy, radiotherapy, and surgery). However, some drawbacks still remain for the current organic photosensitizers such as low singlet oxygen (1O2) quantum yield, poor photostability, inability of absorption in the near-infrared (NIR) region, short excitation wavelength, and limited action radius of singlet oxygen, which will strongly limit the PDT treatment efficiency. As a consequence, the development of efficient photosensitizers with high singlet oxygen quantum yield, strong fluorescent emission in the aggregated state, excellent photostability, NIR excitation wavelength ranging in the biological transparency window, and highly specific targeting to mitochondria is still in great demand for the enhancement of PDT treatment efficiency. In this study, two new two-photon AIEgens TPPM and TTPM based on a rigid D−π–A skeleton have been designed and synthesized. Both AIEgens TPPM and TTPM show strong aggregation-induced emission (AIE) with the emission enhancement up to 290-folds, large two-photon absorption with the two-photon absorption cross section up to 477 MG, and highly specific targeting to mitochondria in living cells with good biocompatibility. They can serve as two-photon bioprobes for the cell and deep tissue bioimaging with a penetration depth up to 150 μm. Furthermore, high 1O2 generation efficiency with high 1O2 quantum yield under white light irradiation has been found for both TPPM and TTPM and high PDT efficiency to HeLa cells under white light irradiation has also been proven. To the best of our knowledge, AIEgens in this work constitute one of the strongest emission enhancements and one of the highest 1O2 generation efficiencies in the reported organic AIEgens so far. The great AIE feature, large two-photon absorption, high specificity to mitochondria in living cells, and high PDT efficiency to living cells as well as excellent photostability and biocompatibility of these novel AIEgens TPPM and TTPM reveal great potential in clinical applications of two-photon cell and tissue bioimaging and image-guided and mitochondria-targeted photodynamic cancer therapy.

# High-Efficiency Air-Stable Colloidal Quantum Dot Solar Cells Based on a Potassium-Doped ZnO Electron-Accepting Layer\_2018

We present here a detailed analysis of the mechanism of photoinduced electron and proton transfer in the planar pyrrole−pyridine hydrogen-bonded system, a model for the photochemistry of hydrogen bonds in DNA base pairs. Two different crossings, an avoided crossing and a conical intersection, are the key steps for forward and backward electron and proton transfer providing to the system photostability against UV radiation by restoring the system in its initial electronic and geometric structure.

# Multifunctional Two-Photon AIE Luminogens for Highly Mitochondria-Specific Bioimaging and Efficient Photodynamic Therapy\_2019

A facile solvothermal method is reported to synthesize highly photoluminescent Ag2Se quantum dots (QDs) with emission at 1300 nm in the second near-infrared window. After surface modification of C18-PMH-PEG, the Ag2Se QDs possess bright photoluminescence, good water-solubility, high colloidal stability and photostability, as well as decent biocompatibility, which are further successfully performed in in vivo deep imaging of organs and vascular structures with high spatial resolution. This new NIR-II fluorescent nanoprobe with small sizes, ideal optical properties, and decent biocompatibility opens up exciting opportunities for future biomedical applications.

# Photoinduced Electron and Proton Transfer in the Hydrogen-Bonded Pyridine−Pyrrole System\_2007

Gold nanorods exhibit intense optical absorption bands in the near-infrared region of principal interest for applications in biomedical optics, which originate from sharp plasmon resonances. This high absorbance, combined with the biochemical inertness and targetability of gold nanoparticles, makes these materials excellent candidates to provide contrast in photoacoustic imaging and for other applications such as the selective hyperthermia of cancer. One issue demoting the potential of gold nanorods as contrast agents in photoacoustic applications is their limited photostability, which falls below relevant permissible exposure limits. In particular, when gold nanorods are resonantly excited by laser pulses in the nanosecond duration regime, there may occur phenomena like reshaping into rounder nanoparticles as well as fragmentation and sublimation, which modify their optical absorption bands and hinder their efficiency of photoacoustic conversion. Here we investigate the influence of nanoparticle size on the photostability and reproducibility of photoacoustic conversion of gold nanorods embedded in biomimetic phantoms. We compare samples containing gold nanorods with different sizes but the same shapes and overall optical densities. We demonstrate clear size effects as the thresholds of optical fluences for nanoparticle deformation improve from below 2 to above 6 mJ/cm2 with nanoparticle miniaturization from 22 to 5 nm effective radii. We interpret these results in terms of a better thermal coupling and faster heat dissipation from smaller nanoparticles to their environment, originating from their larger specific surface area.

# Facile Synthesis of Highly Photoluminescent Ag2Se Quantum Dots as a New Fluorescent Probe in the Second Near-Infrared Window for in Vivo Imaging\_2013

Specific control of photoinduced molecular reactions is desired for various reasons, not least to increase photostability by avoiding harmful, reactive intermediate states. In this paper we will present a way to specifically deactivate the excited-state of merocyanines by selectively addressing additional pathways. The photodynamics for different merocyanines in solution as well as coupled to semiconductor nanoparticles have primarily been investigated by transient absorption spectroscopy. For the free dye, two main fast deactivation pathways exist, one involving an isomerization around the central polymethine chain of the molecule, and the other involving the population of a triplet state. The coupling to a semiconductor nanoparticle provides a way to change photoinitiated dynamics. An ultrafast electron transfer from the dye to the TiO2 nanoparticle takes place, and the isomerization reaction is accelerated by a factor of 20. The population of the triplet state is quenched and does not take place at all. In contrast to the well-known function of TiO2 as photocatalyst, we report here a molecular mechanism that quenches possible degradation pathways and thus might increase the photostability of the adsorbate in a dye/semiconductor system.

# Size Affects the Stability of the Photoacoustic Conversion of Gold Nanorods\_2014

Silicon nanoparticles (SiNPs) have been reported to be synthesized by microwave-assisted methods under high pressure. However, there is still a lack of knowledge about the synthesis of SiNPs via microwave-assisted methods under normal pressure. Here we developed a new, facile, one-pot microwave-assisted method for the synthesis SiNPs (∼4.2 nm) with excellent water solubility under normal pressure by employing glycerol as the solvent. Furthermore, glycerol might be responsible for the photoluminescence quantum yield (PLQY) value up to 47% for the resultant SiNPs. The use of organic solvent could afford less nanoparticle surface defects compared with those prepared in aqueous solution, thus improving the fluorescent efficiency. The as-prepared SiNPs simultaneously featured bright blue-green fluorescence, long lifetime (∼12.8 ns), obvious up-conversion luminescence originating from two-photon absorption, superbly strong photostability, and favorable low toxicity. As a satisfactory probe, the as-synthesized SiNPs were successfully applied in fluorescence imaging of human cervical carcinoma cell lines (HeLa) and zebrafish.

# Quenching of Triplet State Formation by Electron Transfer for Merocyanine/TiO2 Systems\_2008

We report on the synthesis and photophysical and lasing properties of new linear and cross-linked fluorinated polymeric materials doped with two BODIPY chromophores such as PM567 and PM597. The total fluorine content of the matrixes was varied adding to methyl methacrylate (MMA) different volumetric proportions of monomers with increased number of fluorine atoms:  2,2,2-trifluoromethyl methacrylate, 2,2,3,3,3,-pentafluoropropyl methacrylate (PFMA), and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate. The rigidity of the materials was modified adding to PFMA di-, tri-, and tetra-functionalized comonomers such as ethyleneglycol dimethacrylate, pentaerythritol triacrylate, and pentaerythritol tetraacrylate. When the fluorine-modified organic matrixes were transversally pumped at 532 nm, highly stable laser operation with high, not-optimized efficiencies up to 42% was obtained. The highest photostability was recorded for PM597 doped MMA/PFMA 70/30 linear matrix, with no sign of degradation in the laser output after 500 000 pump pulses at 30 Hz, corresponding to an accumulated pump energy of 12 300 GJ/mol. The laser action depended more on the composition of the fluorinated comonomer than on the actual fluorine content with respect to the total weight of the matrix. Narrow line width operation with tuning ranges of up to 37 nm was obtained with both pyrromethene dyes when some of the samples were incorporated into a grazing incidence grating oscillator. Good correlations between the photophysical properties and the lasing behavior have been observed. The remarkable improvement in photostability exhibited by the fluorine-modified organic hold promise in the development of industrial oriented laser applications of organic solid-state materials.

# One-Pot Microwave Synthesis of Water-Dispersible, High Fluorescence Silicon Nanoparticles and Their Imaging Applications in Vitro and in Vivo\_2016

The composite photocatalyst with layered nanoarray structure, CdS-sensitized ZnO nanorod arrays (ZnONRA/CdS) grown on ordered TiO2 nanotube arrays (TiO2NTA), was constructed. The performance of composite photocatalyst toward to hydrogen production from water splitting was investigated. The ZnONRA/CdS composite photocatalyst with the substrate layer of ordered TiO2NTA has the enhanced rate of hydrogen production and the improved photostability. It may be attributed to the one-dimensional structure of TiO2NTA at the bottom of ZnONRA/CdS composite photocatalyst, which provides a direct transfer pathway of photoinjected electrons along the photoanode to enhance charge-collection efficiency and consequently reduce electron–hole recombination.

# Laser and Physical Properties of BODIPY Chromophores in New Fluorinated Polymeric Materials\_2006

Squaraine dyes have excellent photostability with intensive absorption and strong fluorescence in the near-infrared (NIR) region. However, they display a strong tendency to aggregate in aqueous media because of their poor water solubility, often causing fluorescence quenching that severely limits their in vivo applications, especially for detecting or imaging diagnostic enzymes. In this work, an oligo(ethylene glycol)-functionalized squaraine fluorophore has been developed as an NIR-fluorescent probe that can detect and image the activities of a diagnostic enzyme (leucine aminopeptidase) both in vitro and in vivo. The probe shows near-infrared absorption and emission, a low detection limit (0.61 ng/mL), relatively good aqueous solubility, high selectivity, and little toxicity. In addition, the probe herein was successfully used to track endogenous leucine aminopeptidase both in vitro and in vivo with a nude-mouse model.

# Effect of Ordered TiO2 Nanotube Array Substrate on Photocatalytic Performance of CdS-Sensitized ZnO Nanorod Arrays\_2013

Photoacoustic imaging combines both excellent spatial resolution with high contrast and specificity, without the need for patients to be exposed to ionizing radiation. This makes it ideal for the study of physiological changes occurring during tumorigenesis and cardiovascular disease. In order to fully exploit the potential of this technique, new exogenous contrast agents with strong absorbance in the near-infrared range, good stability and biocompatibility, are required. In this paper, we report the formulation and characterization of a novel series of endogenous contrast agents for photoacoustic imaging in vivo. These contrast agents are based on a recently reported series of indigoid π-conjugated organic semiconductors, coformulated with 1,2-dipalmitoyl-sn-glycero-3-phosphocholine, to give semiconducting polymer nanoparticles of about 150 nm diameter. These nanoparticles exhibited excellent absorption in the near-infrared region, with good photoacoustic signal generation efficiencies, high photostability, and extinction coefficients of up to three times higher than those previously reported. The absorption maximum is conveniently located in the spectral region of low absorption of chromophores within human tissue. Using the most promising semiconducting polymer nanoparticle, we have demonstrated wavelength-dependent differential contrast between vasculature and the nanoparticles, which can be used to unambiguously discriminate the presence of the contrast agent in vivo.

# Oligo(ethylene glycol)-Functionalized Squaraine Fluorophore as a Near-Infrared-Fluorescent Probe for the In Vivo Detection of Diagnostic Enzymes\_2018

Low-dimensional halide perovskite (HP) has triggered lots of research attention in recent years due to anisotropic optoelectronic/semiconducting properties and enhanced stability. High-quality low-dimensional HPs via controllable engineering are required to fulfill the encouraging promise for device applications. Here, we introduce, for the first time, postsynthetic ultrasonic-assisted refinement of two-dimensional homologous HPs (OA2PbBr4, OA is octadecylamine). The solution-prepared OA2PbBr4, either in the form of large-sized microcrystal or nanosheet, obtains significantly enhanced crystallinity after ultrasonic treatment. We further show that OA2PbBr4 nanosheets can be used as a template to construct low-dimensional CsPbBr3 with the size and morphology inherited. Importantly, we found the ultrasonic-treated OA2PbBr4 crystals, compared with pristine ones, lead to enhanced optoelectronic properties for the resultant low-dimensional CsPbBr3, as demonstrated by improved photodetection performances, including prolonged charge-carrier lifetime, improved photostability, increased external quantum yield/responsivity, and faster response speed. We believe this work provides novel engineering of low-dimensional HPs beyond the reach of straightforward synthesis.

# Tunable Semiconducting Polymer Nanoparticles with INDT-Based Conjugated Polymers for Photoacoustic Molecular Imaging\_2017

Intracellular oxygen concentration is of primary importance in determining numerous physiological and pathological processes in biological systems. This paper describes the development and application of micrometer-sized oxygen-sensitive fluorescence lipobeads for intracellular measurements of molecular oxygen in J774 murine macrophages. A ruthenium diimine complex [Ru(bpy-pyr)(bpy)2]Cl2 (bpy = 2,2‘-bipyridine, bpy-pyr = 4-(1‘ ‘-pyrenyl)-2,2‘-bipyridine) is used as the oxygen indicator. The indicator exhibits high chemical and photostability and high sensitivity to oxygen. The indicator molecules are immobilized in a phospholipid membrane that coats polystyrene microparticles. The fluorescence of the lipobeads is effectively quenched by molecular oxygen. The fluorescence intensity of the oxygen-sensitive lipobeads is 3 times higher in a nitrogenated solution than in an oxygenated solution. The lipobeads are internalized by murine macrophages through phagocytosis. They maintain their spectral properties for 24 h in living cells when the cells are stored in phosphate-buffered saline at pH 7.4. The photostability, reversibility, and effect of hypoxia, hyperoxia, and oxidative stress on the intracellular level of oxygen in J774 murine macrophages are described.

# Enhancing Optoelectronic Properties of Low-Dimensional Halide Perovskite via Ultrasonic-Assisted Template Refinement\_2017

Five novel near-infrared BODIPY dyes were prepared for improved singlet oxygen generation using thiophene and bromine. Theoretical, optical, photostable, and singlet oxygen generation characteristics of these dyes were assessed. Predicted excitation energies by TDDFT calculations were in good agreement (ΔE ≈ 0.06 eV) with experimental data. All five dyes showed both excitation and emission in the NIR range. In particular, two dyes having sulfur and bromine atoms showed efficient singlet oxygen generation with high photostability.

# Molecular Oxygen-Sensitive Fluorescent Lipobeads for Intracellular Oxygen Measurements in Murine Macrophages\_2001

Quantum technologies could largely benefit from the control of quantum emitters in sub-micrometric size crystals. These are naturally prone to integration in hybrid devices, including heterostructures and complex photonic devices. Currently available quantum emitters in nanocrystals suffer from spectral instability, preventing their use as single-photon sources for most quantum optics operations. In this work we report on the performances of single-photon emission from organic nanocrystals (average size of hundreds of nm), made of anthracene (Ac) and doped with dibenzoterrylene (DBT) molecules. The source has hours-long photostability with respect to frequency and intensity, both at room and at cryogenic temperature. When cooled to 3 K, the 00-zero phonon line shows linewidth values (50 MHz) close to the lifetime limit. Such optical properties in a nanocrystalline environment recommend the proposed organic nanocrystals as single-photon sources for integrated photonic quantum technologies.

# Singlet Oxygen Generation by Novel NIR BODIPY Dyes\_2011

Solid polymer/Si nanocrystal bulk nanocomposites were fabricated from solutions of alkene- and hydride-terminated silicon nanocrystals (NCs) in toluene. The photoluminescence peak position of hydride-terminated SiNCs before polymerization was tuned by photoassisted hydrofluoric acid etching. Optical properties of obtained PMMA/NC hybrids, such as quantum yield, luminescence lifetime, and dispersion factor, were evaluated over time. Photostability of these transparent bulk polymer/SiNC hybrids over months was confirmed. The emission covers the visible to near-infrared range with a quantum yield of ∼30–40% for yellow-red nanocomposites.

# Self-Assembled Nanocrystals of Polycyclic Aromatic Hydrocarbons Show Photostable Single-Photon Emission\_2018

Additives play an important role in modifying the morphology and phase separation of donor and acceptor molecules in bulk heterojunction (BHJ) solar cells. Here, we report triptycene (TPC) as a small-molecule additive for supramolecular control of phase separation and concomitant improvement of the power conversion efficiency (PCE) of PTB7 donor and fullerene acceptor-based BHJ polymer solar cells. An overall 60% improvement in PCE is observed for both PTB7:PC61BM and PTB7:PC71BM blends. The improved photovoltaic (PV) performance can be attributed to three factors: (a) TPC-induced supramolecular interactions with donor:acceptor components in the blends to realize a nanoscale phase-separated morphology; (b) an increase in the charge transfer state energy that lowers the driving force for electron transfer from donor to acceptor molecules; and (c) an increase in the charge carrier mobility. An improvement in efficiency using TPC as a supramolecular additive has also been demonstrated for other BHJ blends such as PBDB-T:PC71BM and P3HT:PCBM, implying the wide applicability of this new additive molecule. A comparison of the photostability of TPC as an additive for PTB7:PCBM solar cells to that of the widely used 1,8-diiodooctane additive shows ∼30% higher retention of PV performance for the TPC-added solar cells after 34 h of AM 1.5G illumination. The results obtained suggest that the approach of using additives that can promote supramolecular interactions to modify the length scale of phase separation between donor and acceptor is very promising and can lead to the development of highly efficient and stable organic photovoltaics.

# Photostable Polymer/Si Nanocrystal Bulk Hybrids with Tunable Photoluminescence\_2016

Fluorescent nanoprobes have become one of the most promising classes of materials for cancer imaging. However, there remain many unresolved issues with respect to the understanding of their long-term colloidal stability and photostability in both biological systems and the environment. In this study, we report long-term-stable near-infrared (NIR) polymer dots for in vivo tumor vasculature imaging. NIR-emitting polymer dots were prepared by encapsulating an NIR dye, silicon 2,3-naphthalocyanine bis(trihexylsilyloxide) (NIR775), into a matrix of polymer dots, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), using a nanoscale precipitation method. The prepared NIR polymer dots were sub-5 nm in diameter, exhibited narrow-band NIR emission at 778 nm with a full width at half-maximum of 20 nm, and displayed a large Stokes shift (>300 nm) between the excitation and emission maxima. In addition, no significant uptake of the prepared NIR polymer dots by either human glioblastoma U87MG cells or human non-small cell lung carcinoma H1299 cells was detected. Moreover, these NIR polymer dots showed long-term colloidal stability and photostability in water at 4 °C for at least 9 months, and were able to image vasculature of xenografted U87MG tumors in living mice after intravenous injection. These results thus open new opportunities for the development of whole-body imaging of mice based on NIR polymer dots as fluorescent nanoprobes.

# Triptycene as a Supramolecular Additive in PTB7:PCBM Blends and Its Influence on Photovoltaic Properties\_2018

A series of deep red fluorescent dyes (CR1 to CR3) was developed via introduction of a coumarin moiety into the rhodamine molecular skeleton. The novel dyes possessed the individual advantages of coumarin and rhodamine derivatives, and the emission wavelength was extended to the deep red region (>650 nm) due to the extension of fused-ring conjugate structure simultaneously. To illustrate its value, we designed and conveniently synthesized a series of novel deep red bioimaging dyes (CR1E to CR3E) by esterification of CR1 to CR3, which could selectively stain mitochondria. They were superior to the MitoTrackers for mitochondrial staining in terms of large Stokes shift, excellent contrast for imaging, high photostability, and low cytotoxicity. Furthermore, the fluorescence of the coumarin moiety and rhodamine-like fluorophore could be switched like classical rhodamine. Thus, they could be used as an effective platform in constructing fluorescence sensors. Based on this fact, we constructed a novel ratiometric sensor (CR1S) for Hg2+ with good selectivity that could be successfully applied to the imaging of Hg2+ in living A549 cells. This design strategy is straightforward and adaptable to various deep red dyes and sensing platforms by simply introducing different fluorophores.

# Long-Term-Stable Near-Infrared Polymer Dots with Ultrasmall Size and Narrow-Band Emission for Imaging Tumor Vasculature in Vivo\_2015

High quality and facile DNA functionalized quantum dots (QDs) as efficient fluorescence nanomaterials are of great significance for bioimaging both in vitro and in vivo applications. Herein, we offer a strategy to synthesize DNA-functionalized Zn2+ doped CdTe QDs (DNA-QDs) through a facile one-pot hydrothermal route. DNA is directly attached to the surface of QDs. The as-prepared QDs exhibit small size (3.85 ± 0.53 nm), high quantum yield (up to 80.5%), and excellent photostability. In addition, the toxicity of QDs has dropped considerably because of the Zn-doping and the existence of DNA. Furthermore, DNA has been designed as an aptamer specific for mucin 1 overexpressed in many cancer cells including lung adenocarcinoma. The aptamer-functionalized Zn2+ doped CdTe QDs (aptamer-QDs) have been successfully applied in active tumor-targeted imaging in vitro and in vivo. A universal design of DNA for synthesis of Zn2+ doped CdTe QDs could be extended to other target sequences. Owing to the abilities of specific recognition and the simple synthesis route, the applications of QDs will potentially be extended to biosensing and bioimaging.

# Coumarin- and Rhodamine-Fused Deep Red Fluorescent Dyes: Synthesis, Photophysical Properties, and Bioimaging in Vitro\_2013

The synthesis of water-soluble near-infrared (NIR)-emitting quantum dots (QDs) in aqueous solution has received much attention recently. However, the stabilizer 3-mercaptopropionic acid, commonly used in the synthesis of NIR-emitting QDs, is notorious for its toxicity and awful odor. Here we chose thiol ligand N-acetyl-l-cysteine (NAC) as the ideal stabilizer and have successfully employed it to synthesize high-quality NIR-emitting CdTe/CdS QDs in a one-step process via a simple hydrothermal route. NAC possesses favorable properties such as nontoxic, nonvolatile, inexpensive, and good water-solubility. Our as-prepared NIR-emitting CdTe/CdS QDs exhibit high photoluminescence quantum yields (45−62%), narrow full-width at half-maximum, and high photostability, thanks to the formation of a protective CdS shell on the CdTe core through the decomposition of NAC in the hydrothermal route under high temperature. The prepared QDs can be applied for bioimaging due to its excellent water-solubility and biological compatibility. The core/shell structure of the NIR-emitting CdTe/CdS QDs was verified by X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy, selected area electron diffraction, and X-ray powder diffraction. The formation mechanism of these QDs is discussed in detail.

# One-Pot Synthesized Aptamer-Functionalized CdTe:Zn2+ Quantum Dots for Tumor-Targeted Fluorescence Imaging in Vitro and in Vivo\_2013

In this paper we present a broad overview of the class of insecticides known as synthetic pyrethroids. The discussion includes a summary of agricultural and urban pyrethroid use patterns and trends, pyrethroid chemical structure and properties, the significance of photostability to pyrethroid environmental fate, and hydrophobicity, persistence and relative aquatic toxicity as compared to other pesticides. Finally we provide a brief summary of California's regulatory response to recent detections of pyrethroids in aquatic sediments and a discussion of scientific and regulatory issues associated with ongoing pyrethroid aquatic exposure assessments and mitigation efforts.

# Synthesis and Characterization of High-Quality Water-Soluble Near-Infrared-Emitting CdTe/CdS Quantum Dots Capped by N-Acetyl-l-cysteine Via Hydrothermal Method\_2008

The fabrication of novel magnetofluorescent nanoparticles (NPs) by complexation of zinc ions present on the surface of a zinc ferrite nanoparticle (ZnFe2O4 NP) with 8-hydroxy-2-quinolinecarboxaldehyde (HQCald) is reported. The as-prepared HQCald-complexed ZnFe2O4 NPs showed good quantum yield (3.62%), high photostability, considerable excited-state lifetime (5.31 ns), and high saturation magnetization (12.7 emu/g). These magnetofluorescent NPs demonstrated bioimaging capability at both the ensemble- and single-particle levels and in vitro magnetic targeting. Moreover, the pronounced antiproliferative efficacy of these NPs against cancer cells, with appropriate targeting strategies, can lead to potential cancer theranostics.

# Synthetic Pyrethroid Use Patterns, Properties, and Environmental Effects\_2008

Carbon dots (CDs) with low biotoxicity, high photostability, and well-controlled size are highly desirable imaging agents for optical bioimaging. However, most of the CDs triggered by ultraviolet/blue light present visible/first near-infrared emissions shorter than 820 nm, impairing their imaging applications in vivo by low penetration depth. Hence, developing novel CD-based materials with second near-infrared (NIR-II) emission located in 1000–1700 nm region is an urgent task. Here, a novel NIR-II-emitting CD-based nanoprobe triggered by 808 nm laser is developed. The designed CDs with 900–1200 nm luminescence possess high quantum yield (QY-0.4%) and high biocompatibility, which have proven to be effective probes for in vivo NIR-II bioimaging. Notably, nearly 65% CDs are excreted from mouse urine within 6 h, demonstrating the rapid renal clearance of CDs. Furthermore, the designed CDs also exhibit high photothermal efficiency (30.6%), making them ideal materials for thermal ablation of cancer. Our findings pave the way of designing a multifunctional CD-based theranostic platform for simultaneously integrating the advanced NIR-II bioimaging and photothermal therapy of cancer.

# Surface-Complexed Zinc Ferrite Magnetofluorescent Nanoparticles for Killing Cancer Cells and Single-Particle-Level Cellular Imaging\_2018

The photophysics of a complex between cucurbit[7]uril (CB7) and rhodamine 6G (R6G) was investigated using single-molecule spectroscopy. On the basis of the distribution of fluorescence intensity, two stable conformations of the CB7/R6G complex were identified. Both exhibit enhanced fluorescence relative to R6G alone. The two conformations are attributed to a flexible inclusion complex of R6G in CB7. Our single-molecule measurements also indicate that the photostability of R6G upon complex formation improves by 13× as opposed to 1.5× reported from ensemble measurements. The simplicity of using CB7 to enhance the fluorescence performance of a fluorophore makes it a promising strategy to deliver better probes for single-molecule spectroscopy in physical and life sciences research.

# Theranostic Carbon Dots with Innovative NIR-II Emission for in Vivo Renal-Excreted Optical Imaging and Photothermal Therapy\_2019

A novel nanocomposite, silicon–carbon-based dots@dopamine (Si-CDs@DA) was prepared using (3-aminopropyl) triethoxysilane, glycerol, and dopamine as raw materials via a rapid microwave-assisted irradiation. This type of Si-CDs@DA exhibited ultrabright fluorescence emission (quantum yield of 12.4%) and could response to Ag+ selectively and sensitively. Moreover, the obtained Si-CDs@DA can be further applied in sensing intracellular Ag+ and cell imaging, because of its photostability, salt stability, and low cytotoxicity. This study provides a simple and efficient approach for preparing novel Ag+ fluorescent probes, which could expand the application of carbon nanomaterials in designing related biosensors.

# Cucurbit[7]uril Induces Superior Probe Performance for Single-Molecule Detection\_2007

Heterogeneous photocatalysis is a promising strategy for addressing the worldwide environmental pollution and energy shortage issues. However, unlike TiO2 with good photostability, the intrinsic drawback of photoinduced decomposition, i.e., photocorrosion, of semiconductors significantly challenges durable photocatalysis. In this review, the photocorrosion mechanisms of typical semiconductors and different characterization methods proposed for monitoring the photocorrosion process of semiconductor-based composite photocatalysts are elaborated. Dedicated emphasis is put on the strategies for improving the anti-photocorrosion property of semiconductor-based photocatalysts, including modifying the crystal structure or morphology of semiconductors, doping with heteroatoms, hybridizing with various semiconductors and/or cocatalysts, and regulating the photocatalytic reaction conditions. Finally, we cast a personal prospect on the future development of the rational design of corrosion-controlled semiconductor-based photocatalysts toward versatile photoredox applications.

# Photocorrosion Inhibition of Semiconductor-Based Photocatalysts: Basic Principle, Current Development, and Future Perspective\_2019

Photodynamic therapy (PDT) of hypericin (Hyp) is hampered by poor water solubility and photostability. Incorporation of photosensitizers into nanocarriers has been designed to solve these issues. Herein, SWNH-Hyps nanohybrids were first fabricated by loading hypericin on the surface of single-walled carbon nanohorns (SWNHs) through ??? interaction and exhibited high solubility and stability in aqueous water. SWNH-Hyps could be utilized for a single platform for cancer therapy because it could simultaneously generate enough reactive oxygen species and hyperthermia using light irradiation. Moreover, the SWNHs not only improved water solubility, photostability, and therapy effects of Hyp but also protected it from light degradation. SWNH-Hyps could effectively ablate 4T1 cells by photodynamic/photothermal synergistic therapy upon 590 and 808 nm light irradiations compared with PDT. Furthermore, remarkable tumor cell death as well as tumor growth inhibition was proved via photothermal therapy and PDT of SWNH-Hyps under 590 and 808 nm light irradiations, which demonstrated that synergistic anticancer ability of SWNH-Hyps was better than that of free Hyp in vivo. Such a simple and facile adsorption method improved water solubility of Hyp and then enhanced its therapy effect, which displays that SWNHs can be hopefully used in medicines in the future.

# Preparation of Silicon–Carbon-Based [email protected] and Its Application in Intracellular Ag+ Detection and Cell Imaging\_2015

We report dramatic improvements in the stability and crystallinity arising from partial fluorination of soluble anthradithiophene derivatives. These fluorinated materials still behave as p-type semiconductors but with dramatic increases in thermal and photostability compared to the non-fluorinated derivatives. The triethylsilyl-substituted material forms highly crystalline films even from spin-cast solutions, leading to devices with maximum hole mobility greater than 1.0 cm2/V s. In contrast, the triisopropylsilyl derivative forms large, high-quality crystals that could serve as the substrate for transistor fabrication. For this compound, mobility as high as 0.1 cm2/V s was measured on the free-standing crystal.

# Hypericin-Loaded Carbon Nanohorn Hybrid for Combined Photodynamic and Photothermal Therapy in Vivo\_2019

Promoting a drug inclusion proportion in hydrophobic cavity of β-cyclodextrin using simple methods is a highly ambitious task. Herein, we report the crowning β-cyclodextrins formed by intramolecular hydrogen bonding interaction, which has greatly prolonged the cavity depth of β-cyclodextrin, and therefore further efficiently improved the inclusion proportion to complex drug molecule (vitamin E). Furthermore, the self-assembly behaviors, controllable release, and antioxidant properties of vitamin E embedded into the cavity of crowning β-cyclodextrins was investigated, and host–guest inclusions exhibited temperature-responsive controlled release, excellent antioxidant activity, and photostability.

# Chromophore Fluorination Enhances Crystallization and Stability of Soluble Anthradithiophene Semiconductors\_2008

We report facile one-pot synthesis of water-soluble green fluorescent gold nanoclusters (AuNCs), capped with 8-mercapto-9-propyladenine. The synthesized AuNCs were characterized by Fourier transform infrared (FTIR), powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), 1H NMR, and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. These nanoclusters show high photostability and biocompatibility. We observed that AuNCs stain cell nuclei with high specificity, where the mechanism of AuNC uptake was established through pathway-specific uptake inhibitors. These studies revealed that cell internalization of AuNCs occurs via a macropinocytosis pathway.

# Construction of Crowning β-cyclodextrin with Temperature Response and Efficient Properties of Host–Guest Inclusion\_2018

We synthesized colloidal InP/ZnS seeded CdS tetrapods by harnessing the structural stability of the InP/ZnS seed nanocrystals at the high reaction temperatures needed to grow the CdS arms. Because of an unexpected Type II band alignment at the interface of the InP/ZnS core and CdS arms that enhanced the occurrence of radiative excitonic recombination in CdS, these tetrapods were found to be capable of exhibiting highly efficient multiexcitonic dual wavelength emission of equal intensity at spectrally distinct wavelengths of ∼485 and ∼675 nm. Additionally, the Type II InP/ZnS seeded CdS tetrapods displayed a wider range of pump-dependent emission color-tunability (from red to white to blue) within the context of a CIE 1931 chromaticity diagram and possessed higher photostability due to suppressed multiexcitonic Auger recombination when compared to conventional Type I CdSe seeded CdS tetrapods. By employing time-resolved spectroscopy measurements, we were able to attribute the wide emission color-tunability to the large valence band offset between InP and CdS. This work highlights the importance of band alignment in the synthetic design of semiconductor nanoheterostructures, which can exhibit color-tunable multiwavelength emission with high efficiency and photostability.

# Purine-Stabilized Green Fluorescent Gold Nanoclusters for Cell Nuclei Imaging Applications\_2014

The novel hydrophobic luminescent copolymer P(Ir-TFEMA) was developed as an online dissolved-oxygen (DO) sensor. The phosphorescent moiety of cyclometalated iridium(III) complex exhibits red emission near 650 nm with a large Stokes shift of about 245 nm and minimal optical interference from the fermentation system. The covalent incorporation of the chromophore into the polymeric matrix rather than physical doping was used to avoid phase-separation and leaching problems. The low molar ratio between the introduced chromophore and polymeric matrix within the range of 1:135–1:250 was confirmed to have little influence on the luminescence response ability. To assess its potential utility, this copolymer was applied to the online monitoring of DO during the cephalosporin C fermentation process. The screen-printing technique was utilized as a rapid and reliable automatic approach to preparing sensor films with good photostability and fatigue resistance, showing promise in bioprocess monitoring as a low-cost DO indicator for high-throughput microbioreactors.

# Efficient Color-Tunable Multiexcitonic Dual Wavelength Emission from Type II Semiconductor Tetrapods\_2014

The photooxidation of water into O2 has been identified as the barrier of water-splitting, and light-driven water oxidation catalysts have been intensively explored to develop highly active water splitting materials. Despite the fascinating advantages for photocatalytic water oxidation, such as abundance in nature, inexpensiveness, low toxicity, thermo/photostability, and suitable electronic band structures, hematite α-Fe2O3 is a poor photocatalyst for water oxidation due to its short exciton lifetime and hole diffusion length, weak carrier mobility, and shallow sunlight penetration depth. In this work, we have synthesized Pt nanoparticles decorated Pt2+-doped α-Fe2O3 nanoplates (Pt/Pt-Fe2O3 NPs) by a one-step solvothermal route which exhibit the enhanced photoactivity and photostability for water oxidation. The introduction of the Pt into the α-Fe2O3 by the means of elemental doping and nanoparticle decoration accounts for the enhanced performance. The doping of Pt2+ into α-Fe2O3 improves the isolation efficiency of the photoinduced carriers which remarkably increases the lifespan of hole carriers, and the adherence of metal Pt nanoparticles to the surface of α-Fe2O3 leads to formation of Schottky barriers at the interface which effectively impedes the combination of photogenerated electrons and holes.

# Screen-Printed Red Luminescent Copolymer Film Containing Cyclometalated Iridium(III) Complex as a High-Permeability Dissolved-Oxygen Sensor for Fermentation Bioprocess\_2013

We report up-conversion emission from an aqueous solution of YVO4:Yb3+,Er3+ nanocrystals synthesized by an original method that produces nanoparticles with excellent crystallinity and no porosity. We show that these YVO4:Yb3+,Er3+ nanocrystals are not very sensitive to nonradiative relaxations, leading to a high green-to-red emission ratio of 6.3. Using a comparison with YVO4:Eu3+ particles, we determined the quantum yield of the up-conversion emission of the aqueous YVO4:Yb3+,Er3+ dispersion to be 0.09 ± 0.04% for an excitation intensity of only 0.55 kW·cm−2 at 970 nm. Furthermore, single YVO4:Yb,Er particles with an estimated size down to 10 nm can be detected using a wide-field microscope under a 970 nm, 8 kW·cm−2 excitation. Because of their unexpectedly high up-conversion emission without intermittency, their water dispersibility, and their photostability, YVO4:Yb3+,Er3+ nanoparticles are highly appropriate both for single-biomolecule and for in vivo imaging.

# One-Step Solvothermal Formation of Pt Nanoparticles Decorated Pt2+-Doped α-Fe2O3 Nanoplates with Enhanced Photocatalytic O2 Evolution\_2019

Fluorescence is a versatile tool for spectroscopic investigations and imaging of dynamic processes and structures across various scientific disciplines. The photophysical performance, that is, signal stability and signal duration, of the employed fluorophores is a major limiting factor. In this Letter, we propose a general concept to covalently link molecules, which are known for their positive effect in photostabilization, to form a combined photostabilizer with new properties. The direct linkage of two (or more) photostabilizers will allow one to obtain combined or synergetic effects in fluorophore stabilization and can simplify the preparation of imaging buffers that would otherwise require a mixture of photostabilizers for optimal performance. This concept was explored by synthesizing a molecule with a reducing and oxidizing moiety that is referred to as internal ROXS or “iROXS”. Using single-molecule fluorescence microscopy, inter- and intramolecular healing of iROXS was observed, that is, strongly reduced blinking and increased photostability of the cyanine fluorophore Cy5. Moreover, it is shown that a covalently coupled photostabilizer can replace a mixture of molecules needed to make a functional photostabilizing ROXS buffer and might hence represent the new standard for defined and reproducible imaging conditions in single-molecule experiments. In self-healing fluorophores with intramolecular triplet-state quenching, an unprecedented photostability increase of >100-fold was obtained when using iROXS, which is even competitive with solution-based healing. Control experiments show that the oxidizing part of the iROXS molecule, an aromatic nitro group, dominates the healing process. The suggested synthetic concept and the proof-of-concept experiments represent the starting point for the quest to identify optimal combinations of linked photostabilizers for various fluorescence applications.

# High Up-Conversion Efficiency of YVO4:Yb,Er Nanoparticles in Water down to the Single-Particle Level\_2010

Nonconjugated red fluorescent polymers have been increasingly studied to improve the biocompatibility and penetration depth over conventional fluorescent materials. However, the accessibility of such polymers remains challenging due to the scarcity of nonconjugated fluorophores and lacking relevant mechanism of red-shifted fluorescence. Herein, we discovered that the combination of hydrogen bonding and π–π stacking interactions provides nonconjugated poly(amide-imide) with a large bathochromic shift (>100 nm) from blue-green fluorescence to red emission. The amphiphilic PEGylated poly(amide-imide) derived from in situ PEGylation self-assembled into nanovesicles in water, which isolated the aminosuccinimide fluorophore from the solvents and suppressed the hydrogen bonds formation between aminosuccinimide fluorophores and water. Therefore, the fluorescence of PEGylated poly(amide-imide) in water was soundly retained. Furthermore, the strong hydrogen bonding and hydrophobic interactions with water provided PEGylated poly(amide-imide) with a reversible thermoresponsiveness and presented a concentration-dependent behavior. Finally, accompanied by the excellent biostability and photostability, PEGylated poly(amide-imide) exhibited as a good candidate for cell imaging.

# The Power of Two: Covalent Coupling of Photostabilizers for Fluorescence Applications\_2014

Several copolymers of fluorinated acrylates and methacrylates with unfluorinated acrylates, methacrylates and vinyl ethers have been synthesized, and thin films of these materials have been evaluated in terms of chemical stability under accelerated photoaging conditions. Either commercially available or specifically synthesized fluorinated acrylic comonomers, such as methyl α-trifluoromethyl. acrylate (MTFMA) and ethyl 3,3-difluoro-2-methylpropenoate (MFPE), were employed. If suitably selected, these fluoroacrylates can allow both control on the macromolecular structure and tailoring of material properties that are relevant for coating applications, such as film-forming behavior, adhesion, water repellency and intrinsic photostability. The photodegradation behavior of partially fluorinated copolymers and of their unfluorinated analogues was compared, and specific structural features responsible for crosslinking and/or bond scission reactions were analysed.

# Self-Assembling Nonconjugated Poly(amide-imide) into Thermoresponsive Nanovesicles with Unexpected Red Fluorescence for Bioimaging\_2019

Incorporation of chromophores into a polymer chain results in prominent photoreversibility and fatigue resistance, photostability over the long term, and restriction of the internal conversion (IC). Here, we report the copolymerization of two photoactive monomers with methyl methacrylate via emulsion polymerization in order to obtain photoswitchable dual-color fluorescent nanoparticles. For this purpose, azocarbazole ethyl acrylate (AzoCzEA) and spiropyran ethyl acrylate (SPEA) were synthesized and the fluorescence polymeric latex nanoparticles were prepared correspondingly. FT-IR and 1HNMR spectra were used to confirm the structure of novel fluorescent AzoCzEA. UV–vis studies of the obtained nanoparticles displayed the spectral features of both AzoCzEA and SPEA under stimuli-irradiation and inclusion of these chromophores into the polymer particles. DSC analysis revealed an increase in Tg of the prepared copolymer, indicating covalently incorporation of the photoactive monomers into the polymer chains. The optimum ratio of two chromophores to achieve complete quenching and highest energy transfer was determined by UV–vis spectroscopy. DLS and SEM results demonstrated particle size distribution of 40–80 nm with spherical morphology. Fluorescence spectra revealed remarkable fluorescence resonance energy transfer (FRET) from AzoCzEA to SPEA after UV irradiation at 365 nm and dual-color characteristic of the prepared nanoparticles. Besides, an enhancement in the photoreversibility, photostability, prevention of IC, dye leakage, and aggregation were studied elaborately. The obtained results were attributed to the involvement of such chromophores into the polymeric matrix via covalent bonding. Labeling and tracking of living cells and rewriteable patterning are potential applications for such dual-color fluorescent nanoparticles.

# Design of Fluorinated Acrylic-Based Polymers as Water Repellent, Intrinsically Photostable Coating Materials for Stone\_2001

In this paper, a novel biocompatible and long-life lysosome labeling and tracking method based on dye entrapped silica nanoparticles (DSiNPs) has been put forward. Through colocalization studies using LysoTracker Green as the standard lysosome marker, it has been demonstrated that DSiNPs selectively accumulated in lysosomes of Hela cells and the photostability of DSiNPs associated with lysosomes was detectable, at least, 30 times as long as that of LysoTracker Green involved in lysosomes. By comparison with LysoTracker Green and Alexa 488-dextran, the fluorescence of DSiNPs could be detected over a 5-day postrecultivation period and the staining pattern in lysosomes could be well retained after cell fixation and permeabilization. In addition, results from MTT assays showed that DSiNPs did not affect the viability of Hela cells at the concentration for lysosome labeling. Primary applications of DSiNPs were then further performed in lysosome tracking in chloroquine-treated Hela cells, and lysosome labeling of differnet cell lines, including MCF-7 cells, MEAR cells, and MSC cells. These results indicated that DSiNPs, therefore, can be used as a biocompatible, long-life, and highly photostable lysosome marker for lysosome-related studies.

# FRET Phenomenon in Photoreversible Dual-Color Fluorescent Polymeric Nanoparticles Based on Azocarbazole/Spiropyran Derivatives\_2015

Here we describe single-particle imaging studies conducted on the conjugated polyelecrolyte poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] (MPS-PPV) supported on SiO2 nanoparticles. The particles are subjected to a time-programmed sequence involving addition and removal of different additives, including excited-triplet-state quenchers and scavengers of singlet oxygen as well as ground-state oxygen. Our studies show that these additives enhance the emission intensity and photostability of the nanoparticles and may further repair photodamaged conjugated polymer. The ability to monitor the emission from individual particles along multiple cycles under a range of conditions provides a mechanistic insight into the action of these additives.

# Nanoparticle-Based Biocompatible and Long-Life Marker for Lysosome Labeling and Tracking\_2010

The development of green alternatives for petroleum-based plastics is essential for the protection of our environment and its ecosystems. Here, we demonstrate broadband UV-blocking, highly transparent composite nanopaper films from a waste source of cellulose nanofibrils with embedded tunable UV-absorbing nanoparticles (NPs) from ethyl cellulose. These functional nanopaper films are highly transparent, selectively block UV light, and show excellent photostability, therefore with great potential as high-performance, renewable, sustainable, and biodegradable materials for photoprotection applications. Moreover, the integration of functionalized NPs from ethyl cellulose into nanopaper is a platform for novel advanced sustainable materials with a myriad of functionality.

# Enhancing the Emissive Properties of Poly(p-phenylenevinylene)-Conjugated Polyelectrolyte-Coated SiO2 Nanoparticles\_2011

In vivo monitoring of the biodistribution and activation of prodrugs is urgently required. Near infrared (NIR) fluorescence-active fluorophores with excellent photostability are preferable for tracking drug release in vivo. Herein, we describe a NIR prodrug DCM-S-CPT and its polyethylene glycol–polylactic acid (PEG-PLA) loaded nanoparticles as a potent cancer therapy. We have conjugated a dicyanomethylene-4H-pyran derivative as the NIR fluorophore with camptothecin (CPT) as the anticancer drug using a disulfide linker. In vitro experiments verify that the high intracellular glutathione (GSH) concentrations in tumor cells cause cleavage of the disulfide linker, resulting in concomitantly the active drug CPT release and significant NIR fluorescence turn-on with large Stokes shift (200 nm). The NIR fluorescence of DCM-S-CPT at 665 nm with fast response to GSH can act as a direct off–on signal reporter for the GSH-activatable prodrug. Particularly, DCM-S-CPT possesses much better photostability than ICG, which is highly desirable for in situ fluorescence-tracking of cancer chemotherapy. DCM-S-CPT has been successfully utilized for in vivo and in situ tracking of drug release and cancer therapeutic efficacy in living animals by NIR fluorescence. DCM-S-CPT exhibits excellent tumor-activatable performance when intravenously injected into tumor-bearing nude mice, as well as specific cancer therapy with few side effects. DCM-S-CPT loaded in PEG-PLA nanoparticles shows even higher antitumor activity than free CPT, and is also retained longer in the plasma. The tumor-targeting ability and the specific drug release in tumors make DCM-S-CPT as a promising prodrug, providing significant advances toward deeper understanding and exploration of theranostic drug-delivery systems.

# Fully Biobased Highly Transparent Nanopaper with UV-Blocking Functionality\_2019

Detailed studies on the live cell uptake properties of a dinuclear membrane-permeable RuII cell probe show that, at low concentrations, the complex localizes and images mitochondria. At concentrations above ∼20 μM, the complex images nuclear DNA. Because the complex is extremely photostable, has a large Stokes shift, and displays intrinsic subcellular targeting, its compatibility with super-resolution techniques was investigated. It was found to be very well suited to image mitochondria and nuclear chromatin in two color, 2C-SIM, and STED and 3D-STED, both in fixed and live cells. In particular, due to its vastly improved photostability compared to that of conventional SR probes, it can provide images of nuclear DNA at unprecedented resolution.

# In Vivo and in Situ Tracking Cancer Chemotherapy by Highly Photostable NIR Fluorescent Theranostic Prodrug\_2014

Approximately 3 g of water-soluble AgInS2/ZnS core/shell quantum dots (AIS/ZnS QDs) with a maximum photoluminescence quantum yield of up to 39.1% was synthesized in an aqueous solution of gelatin and thioglycolic acid (TGA). The composition of the AIS QDs could be readily adjusted by controlling the molar ratio of the starting Ag/In precursors in the reaction solution, which leads to a tunable emission ranging from 535 to 607 nm. The as-prepared core/shell QDs exhibit excellent photostability and water/buffer stability. More importantly, these cadmium-free hydrophilic AIS/ZnS core/shell QDs are biocompatible and can be directly utilized in cancer cell imaging.

# Multimodal Super-resolution Optical Microscopy Using a Transition-Metal-Based Probe Provides Unprecedented Capabilities for Imaging Both Nuclear Chromatin and Mitochondria\_2017

Pyrethroids are synthetic pesticides with a chemical structure based on natural pyrethrins to enhance photostability and insecticidal activity. They are the family of chiral pesticides with a large number of stereoisomers. Enantiomers of pyrethroids have different biological activity and toxicity against mammals so the development of reliable chiral analytical methods for the determination of individual stereoisomers is indispensable. Several techniques have been developed for this purpose including gas chromatography, high performance liquid chromatography (HPLC), and so forth. In this chapter, the analysis of synthetic pyrethroids by HPLC with chiral stationary phases including some historical background of this line of research is described.

# Scaling up the Aqueous Synthesis of Visible Light Emitting Multinary AgInS2/ZnS Core/Shell Quantum Dots\_2015

An overview of the applications of luminescent transition metal complexes to sensor technology is presented. In addition to general considerations, a number of specific systems are discussed including oxygen, pH, carbon dioxide, temperature, and immunoassay sensors. Applications of the complexes to molecular probes are also covered including chirality and conformational proves, water exposure sensors, and dynamic probes. Problem areas such as photostability, excitability, immobilization chemistry, the existence multiple responses in the same molecule, and substrate-support interactions are discussed. Also covered is the very difficulty problem of unambiguously interpreting the complex kinetic and chemical behavior of real sensor systems.

# Applications of Luminescent Transition Metal Complexes to Sensor Technology and Molecular Probes\_1997

Lipid droplets are highly associated with obesity, diabetes, inflammatory disorders, and cancer. A reliable two-photon dye for specific lipid droplets imaging in live cells and live tissues at ultralow concentration has rarely been reported. In this work, four new aggregation-induced emission luminogens (AIEgens) based on the naphthalene core were designed and synthesized for specific two-photon lipid droplet staining. The new molecules, namely, NAP AIEgens, exhibit large Stokes shift (>110 nm), high solid-state fluorescence quantum yield (up to 30%), good two-photon absorption cross section (45–100 GM at 860 nm), high biocompatibility, and good photostability. They could specifically stain lipid droplets at ultralow concentration (50 nM) in a short time of 15 min. Such ultralow concentration is the lowest value for lipid droplets staining in live cells reported so far. In vitro and ex vivo two-photon imaging of lipid droplets in live cells and live mice liver tissues were successfully demonstrated. In addition, selective visualization of lipid droplets in live mice liver tissues could be achieved at a depth of about 70 μm. These excellent properties render them as promising candidates for investigating lipid droplet-associated physiological and pathological processes in live biological samples.

# Direct Chiral Separation of Pyrethroid Isomers by HPLC with Chiral Stationary Phases\_2012

Recently, photodynamic therapy (PDT) has attracted significant attention as a minimally invasive approach for cancer treatment. Clinical applications of current photosensitizers are often limited by their poor water solubility, low singlet oxygen (1O2) quantum yields, long-term toxicity, instability, and complex nanostructures. Here, we report a rational design of polyhedral oligomeric silsesquioxanes (POSSs)-based porphyrin (PPP5000) used as an intrinsically nanoscale photosensitizer. In this strategy, inorganic 3D rigid block POSSs not only act as antiaggregate units but also provide conjugating reactive sites for further chemical modification. Without an additional carrier and formulation process, PPP5000 intrinsically shows high water solubility (∼40 mg/mL), good PDT efficiency, and more excellent anticancer performance compared to tetra(hydroxyphenyl)porphyrin (the parent compound of m-THPC, Foscan). Considering the organic nature of porphyrin and the biodegradable property of inorganic POSS scaffolds at physiological conditions, the present work may lead to a new generation of biodegradable and intrinsic PDT agents with overall performance superior to conventional agents in terms of 1O2 production efficiency, water solubility, structurally stability, photostability, and biocompatibility.

# Specific Two-Photon Imaging of Live Cellular and Deep-Tissue Lipid Droplets by Lipophilic AIEgens at Ultralow Concentration\_2018

The abnormal location or generation of superoxide radical anion (O2•–) are implicated in many diseases, including cancers; thus, development of an efficient method to detect O2•– is of great importance. Inspired by the fluorophore-governed selective manner to O2•– and peroxynitrite (ONOO–) of previously reported phosphinate-based fluorescence probes, in this contribution, a phosphinothioate-containing probe, TPP, was designed. The probe exhibited easy accessibility through a one-step sequence and good photostability and biocompatibility. Interestingly, TPP showed high specificity and sensitivity to O2•– over other reactive oxygen species/nitrogen species including ONOO–. Furthermore, with the assistance of two-photon microscopy, TPP was successfully applied for imaging endogenous O2•– in live cells and tissues.

# Nanoscale Organic–Inorganic Hybrid Photosensitizers for Highly Effective Photodynamic Cancer Therapy\_2017

A new one-step synthesis of formylated poly[methyl(phenyl)silanediyl] (PMPSi) is reported. The aldehyde groups were incorporated into the parent polymer by the reaction with dichloromethyl methyl ether in the presence of Lewis acid (SnCl4). The reaction takes place via an unstable aryl(methoxy)methyl chloride intermediate. The new procedure is an important simplification of the known four-step synthesis of the poly[(formylphenyl)methylsilanediyl] via chloromethylation in the first step. The presence and reactivity of aldehyde groups in the polymer were proved by means of 1H NMR, UV−vis, and FT IR spectroscopies. The reduction in relative molecular weight of the parent polysilane after reaction was not so pronounced as in the multistep synthesis. Model compounds N-benzylidene-1-aminopyrene, N-benzylidene-4-phenylaniline, and N-benzylidene-4-phenylazoaniline were synthesized for spectral characterization of the substituted polysilanes. The π-conjugated systems (pyrene, biphenyl, azobenzene) were attached to the σ-conjugated polysilane backbone. Photophysical properties, photostability, charge photogeneration, and photoluminescence of these materials were studied. Single- and double-layer light-emitting devices (LEDs) with emission in visible spectral region were fabricated. Their spectral and electrical characteristics were studied. Electroluminescence efficiency in double-layer LEDs reached the value of 0.03−0.06% and was more than 1 order of magnitude higher than that in single-layer devices (∼0.005%). Modified polysilanes exhibited better photostability than PMPSi and are particularly intended for the use in multilayer or blend devices.

# Two-Photon Fluorescence Probe for Selective Monitoring of Superoxide in Live Cells and Tissues\_2019

Biocompatible organic dyes emitting in the near-infrared are highly desirable in fluorescence imaging techniques. Herein we report a synthetic approach for building novel small peri-guanidine-fused naphthalene monoimide and perylene monoimide chromophores. The presented structures possess near-infrared absorption and emission, high photostability, and good water solubility. After a fast cellular uptake, they selectively stain mitochondria with a low background in live and fixed cells. They can be additionally modified in a one-step reaction with functional groups for covalent labeling of proteins. The low cytotoxicity allows a long time exposure of live cells to the dyes without the necessity of washing. Successful application in localization super-resolution microscopy was demonstrated in phosphate-buffered saline without any reducing or oxidizing additives.

# New Synthesis, Electroluminescence, and Photophysical Properties of Poly[(formylphenyl)methylsilanediyl] and Its Derivatives\_2002

In this work, we have prepared a p-type semiconductor of Cu2O decorated with MoS2 nanosheets as cocatalyst for efficient solar hydrogen production under visible light. Results show that Cu2O decorated with 1.0 wt % MoS2 presents the maximum reduction photocurrent density of 0.17 mA cm–2, which is 7-fold higher than pristine Cu2O. Furthermore, the as-prepared MoS2@Cu2O exhibits remarkable photostability with only 7% loss of its original photocurrent after 9 h of continuous work. The excellent performance of MoS2@Cu2O is ascribed to the introduction of active sites of MoS2 nanosheets as cocatalyst to the surface of Cu2O nanoparticles, which activates the photocatalyst by lowering the electrochemical proton reduction overpotential and also inhibits photoinduced corrosion during the measurement.

# Water-Soluble NIR-Absorbing Rylene Chromophores for Selective Staining of Cellular Organelles\_2016

This study aims to improve the photodynamic properties and biological effectiveness of 151-hydroxypurpurin-7-lactone dimethyl ester (G2), a semisynthetic photosensitizer, for the PDT treatment of cancer. The strategy we undertook was by conjugating G2 with aspartic acid and lysine amino acid moieties. The photophysical properties, singlet oxygen generation, distribution coefficiency (Log D in octanol/PBS pH 7.4), and photostability of these analogues and their in vitro bioactivities such as cellular uptake, intracellular localization, and photoinduced cytotoxicity were evaluated. In addition, selected analogues were also investigated for their PDT-induced vasculature occlusion in the chick chorioallantoic membrane model and for their antitumor efficacies in Balb/C mice bearing 4T1 mouse mammary tumor. From the study, conjugation with aspartic acid improved the aqueous solubility of G2 without affecting its photophysical characteristics. G2-Asp showed similar in vitro and in vivo antitumor efficacies compared to the parent compound. Given the hydrophilic nature of G2-Asp, the photosensitizer is a pharmaceutically advantageous candidate as it can be formulated easily for systemic administration and has reduced risk of aggregation in vascular system.

# Cu2O Decorated with Cocatalyst MoS2 for Solar Hydrogen Production with Enhanced Efficiency under Visible Light\_2014

BF2-bridged azafulvene dimers designed to be strong electron-accepting units were selectively synthesized using a bulky base. Single-crystal X-ray diffraction analysis revealed that the high electron-accepting ability of this structure stems from the contribution of the π-conjugation mode of the azafulvene dimer upon formation of B–N coordination bonds. As a result of the low-lying LUMO energy of this electron-accepting unit, the corresponding D–A–D dye exhibits an intense NIR absorption band at 922 nm, which tails up to 1150 nm, while significant absorption bands in the visible region are absent. As a NIR dye this molecule exhibits moreover exceptional photostability and resistance to oxidation by atmospheric oxygen, even in dilute solution.

# Photodynamic Characterization of Amino Acid Conjugated 151-Hydroxypurpurin-7-lactone for Cancer Treatment\_2014

We report a blue dye, coded as R6, which features a polycyclic aromatic hydrocarbon, 9,19-dihydrobenzo[1′,10′]phenanthro[3′,4′:4,5]thieno[3,2-b]benzo[1,10]phenanthro[3,4-d]thiophene, coupled with a diarylamine electron donor and 4-(7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)benzoic acid acceptor. Dye R6 displays a brilliant sapphire color in a sensitized TiO2 mesoporous film with a Co(II/III) tris(bipyridyl)-based redox electrolyte. The R6 based dye-sensitized solar cell achieves an impressive power conversion efficiency of 12.6% under standard air mass 1.5 global, 100 mW cm–2, and shows a remarkable photostability.

# NIR-Absorbing Dye Based on BF2-Bridged Azafulvene Dimer as a Strong Electron-Accepting Unit\_2018

Cyclometalated IrIII complexes are promising candidates for biomedical applications but high cytotoxicity limits their use as imaging and sensing agents. We herein introduce the use of Laponite as carrier for triplet-emitting cyclometalated IrIII complexes. Laponite is a versatile nanoplatform because of its biocompatibility, dispersion stability and large surface area that readily adsorbs functional nonpolar and cationic molecules. These inorganic–organic hybrid nanomaterials mask cytotoxicity, show efficient cell uptake and increase luminescent properties and photostability. By camouflaging intrinsic cytotoxicity, this simple method potentially extends the palette of available imaging and sensing dyes to any metal–organic complexes, especially those that are usually cytotoxic.

# A Stable Blue Photosensitizer for Color Palette of Dye-Sensitized Solar Cells Reaching 12.6% Efficiency\_2018

Thin films of meso-tetra(4-carboxyphenyl)porphyrinato copper(II) (CuTCPP) in conjunction with anatase TiO2 have been formed on cotton fabric. Their self-cleaning properties have been investigated by conducting photocatalytic degradation of methylene blue, coffee and wine stains under visible-light irradiation. CuTCPP/TiO2-coated cotton fabrics showed superior self-cleaning performance when compared to bare TiO2-coated cotton. Furthermore, CuTCPP/TiO2-coated fabrics showed significant photostability under visible-light as compared to free base TCPP/TiO2-coated fabrics. The fabrics were characterized by FESEM, XRD and UV–vis spectroscopy. An insight into the mechanistic aspects of the CuTCPP/TiO2 photocatalysis is also discussed. Visible-light driven self-cleaning cotton based on copper(II) porphyrin/TiO2 catalyst exhibits significant potential in terms of stability and reproducibility for self-cleaning applications.

# Reaching Biocompatibility with Nanoclays: Eliminating the Cytotoxicity of Ir(III) Complexes\_2018

Applications of multiphoton processes in lanthanide-doped nanophosphors (NPs) are often limited by relatively weak and narrow absorbance. Here, the concept of an ultimate photosensitization by aggregation-induced enhanced emission (AIEE) dyes to overcome this limitation is introduced. Because AIEE dyes do not suffer from concentration quenching, they can fully cover the NP surface at high density to maximize absorbance while passivating the surface. This concept is applied to multiphoton down-conversion by quantum cutting. Specifically, coating Yb3+/Tb3+-doped NPs with an AIEE dye designed for efficient energy transfer and attachment to the NPs produces a 2260-fold enhancement of multiphoton down-conversion by quantum cutting with remarkable photostability. In a prototypical application, the quantum cutting of UV photons to near-infrared photons that are matched to the band gap of a silicon solar cell produces an average 4% increase in efficiency under concentrated solar illumination. This provides a general strategy for NP photosensitization that can be applied to both multiphoton up- and down-conversion.

# Photostable Self-Cleaning Cotton by a Copper(II) Porphyrin/TiO2 Visible-Light Photocatalytic System\_2013

Protease represents an important class of biomarkers for disease diagnostics and drug screening. Conventional fluorescence-based probes for in vivo protease imaging suffer from short excitation wavelengths and poor photostability. Upconversion nanoparticles (UCNPs) hold great promise for biosensing and bioimaging because of their deep-tissue excitability, robust photostability, and minimal imaging background. However, producing highly stable and compact biofunctionalized UCNP probes with optimal bioresponsivity for in vivo imaging of protease activities still remains challenging and has not been previously demonstrated. Herein, we report facile preparation of highly compact and stable biofunctionalized UCNPs through peptide-mediated phase transfer for high-sensitive detection of protease in vitro and in vivo. We demonstrate that the polyhistidine-containing chimeric peptides could displace oleic acid molecules capped on UCNPs synthesized in organic solvents and, thereby, directly transfer UCNPs from the chloroform phase to the water phase. The resulting UCNPs possess high stability, programmable surface properties, and a compact coating layer with minimized thickness for efficient luminescence resonance energy transfer (LRET). On the basis of this strategy, we prepared LRET-based UCNP probes with optimal bioresponsivity for in vitro high-sensitive detection of trypsin and in vivo imaging of apoptosis for chemotherapy efficacy evaluation. The reported strategy could be extended to construct a variety of peptide-functionalized UCNPs for various biomedical applications.

# Dramatic Enhancement of Quantum Cutting in Lanthanide-Doped Nanocrystals Photosensitized with an Aggregation-Induced Enhanced Emission Dye\_2018

A turn-on orange-red fluorescent nanosensor based on rhodamine B derivative-functionalized graphene quantum dots (RBD-GQDs) has been successfully synthesized for Fe3+ detection with high sensitivity and selectivity. By connecting with GQDs, the water solubility, sensitivity, photostability, and biocompatibility of RBD are drastically improved. The most distinctive feature of the RBD-GQDs, which sets them apart from other previously reported fluorophores or GQDs, is that they with the detection limits as low as 0.02 μM are demonstrated as a Fe3+ turn-on fluorescent nanosensor in cancer stem cells. Fe3+ binding to such GQDs (RBD-GQDs-Fe3+) with orange-red fluorescence of 43% quantum yield were demonstrated to be the biomarkers for cancer stem cell imaging.

# Compact, Programmable, and Stable Biofunctionalized Upconversion Nanoparticles Prepared through Peptide-Mediated Phase Transfer for High-Sensitive Protease Sensing and in Vivo Apoptosis Imaging\_2015

Mesoporous silica nanoparticles (MSN) and periodic mesoporous organosilica nanoparticles containing bridging benzene (PMOBTB) and ethane (PMOBTE) moieties are synthesized, characterized, and evaluated for application in skin protection from UVA/UVB sun irradiation. Furthermore, the influence of surface functionalization with chelating 3-(2-aminoethylamino)propylsilane and Zn2+ ions on the UV-blocking ability of MSN is evaluated, along with the photostability and capability of the synthesized nanomaterials to carry avobenzone, a known UV-absorbing agent. The obtained results reveal promising characteristics of MSN and PMO materials with regard to their potential for sunscreen applications, which could be beneficial in terms of alleviating concerns about health and environmental hazards of sunscreen ingredients.

# Rhodamine-Functionalized Graphene Quantum Dots for Detection of Fe3+ in Cancer Stem Cells\_2015

Fluorescence imaging is critical for physiological activities and cell biology but limited by the poor solubility, cell compatibility, and permeability. Herein, we develop a novel engineering methodology to prepare biocompatible and penetrable aggregation-induced emission (AIE) nanoparticles with the assistance of flash nanoprecipitation (FNP) technology. On the basis of the donor-π-acceptor (D-π-A) system, the AIE building block of tricyano-methylene-pyridine (TCM) is fine-tuned to long emission wavelength by modulating the π-conjugation bridge and electron-donating group, thereby achieving high solid fluorescent quantum yield, near-infrared (NIR) characteristic, large Stokes shift, and excellent photostability. On the basis of the FNP technology, the amphiphilic saponin solution and TCMN-5 in organic solvent are quickly mixed in the multi-inlet vortex mixer (MIVM), followed by saponin-encapsulation of the hydrophobic AIE nucleation with inhibiting further growth of nanoparticles. The biocompatible amphiphilic saponin such as α-hederin can encapsulate and micellize the AIE TCM fluorophore for efficient cell imaging. The kinetic FNP technology can not only modulate the uniform diameter size, but also distinctly increase the micelle stability when compared to the conventional thermodynamic self-aggregation method, which provides an alternative opportunity for scale-up preparation of drugs and probes in delivery vehicles.

# Mesoporous Silica and Organosilica Nanomaterials as UV-Blocking Agents\_2018

In this study, a series of alcohol-soluble cross-linked block copolymers (BCPs) consisting of poly(n-butyl acrylate) (poly(nBA)) and poly(N-vinyl-1,2,4-triazole) (poly(NVTri)) blocks with different individual functions and lengths are designed and developed. These presynthesized cross-linked BCPs (PBAn–Trim) were, for the first time, revealed to exhibit many advantages in serving as the electron-extraction layer (EEL) for organic photovoltaics (OPVs). The cross-linked BCPs possessed intense ionic functionality, showing well capability to form effective interfacial dipoles at the indium tin oxide interface to facilitate the charge extraction at the corresponding interface. Furthermore, it also consisted a core–shell structure, wherein the polar poly(NVTri) core was well protected by the poly(nBA) shell to endow improved robustness against solvent erosion and thermal/photo inputs. Consequently, the PBA70–Tri30 device yielded a decent power conversion efficiency of 8.03% with a Voc of 0.83 V, much exceeding the performance of the control device without using any EEL. Moreover, this device showed superior thermal stability/photostability. More than 80% of its initial performance was retained after being heated at 60 °C for 1000 h or exposed under continuous illumination (1 sun) for 1000 h, greatly surpassing the lifetime of the control device and the reference device using a common poly[(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) EEL. The results revealed the merit of using cross-linked BCPs in improving the long-term stability of OPVs.

# Saponin-Based Near-Infrared Nanoparticles with Aggregation-Induced Emission Behavior: Enhancing Cell Compatibility and Permeability\_2019

A novel, two-photon probe for the detection of free Mg2+ ions in living cells and live tissues has been developed. The probe can be excited by 880 nm laser photons, emits strong two-photon excited fluorescence in response to Mg2+ ions, can be easily loaded into the cell and tissue, shows high photostability, and can measure the Mg2+ ion concentration without interference by Ca2+ ions in living cells. The intracellular dissociation constant (Kdi) for Mg2+ determined by the two-photon process is 2.5 mM, which is suitable for dynamic Mg2+ concentration measurement. In addition, the probe is capable of imaging endogenous stores of free Mg2+ at a few hundred micrometers depth in live tissues using two-photon microscopy (TPM).

# Alcohol-Soluble Cross-Linked Poly(nBA)n-b-Poly(NVTri)m Block Copolymer and Its Applications in Organic Photovoltaic Cells for Improved Stability\_2018

The aim of this work was to design strategies to improve the performance of solid-state lasers and amplifiers based on perylenediimide (PDI) derivatives as active materials. So, the effect of different types of modifications of the chemical structure of PDIs in their spectral, electrochemical, and laser properties in both solution and PDI-doped polystyrene films at various concentrations has been investigated. In particular, we focused on controlling the wavelength of emission in order to tune the laser wavelength as well as in increasing the amount of PDI in the films in order to decrease the laser thresholds, while keeping a good photostability. Three types of modifications of the chemical structure were investigated:  (a) symmetrical substitution at the imide nitrogen positions (PDI 1); (b) substitution at the bay positions in the PDI core (PDI 4); and (c) modification in the dicarboximide group (PDI 5). All three derivatives were soluble and showed good n-type acceptor ability. Routes b and c led to red shifts in the absorption and photoluminescence (PL) emission, although the PL quantum yield decreased considerably. Amplified spontaneous emission (ASE) was observed in films doped with PDI 1 (λ = 579 nm) and PDI 4 (λ = 599 nm). The best performance, with an ASE threshold of 15 kW/cm2 and a photostability halflife of 31 × 103 pump pulses, was obtained for films doped with 0.75 wt % of PDI 1 (route 1). PDI 1-based materials are among the most photostable reported in the literature and show very-reasonable thresholds. Moreover, these materials are particularly interesting in the field of data communications based on polymer optical fibers because they emit at wavelengths close to 570 nm, which constitutes the second low-loss transmission window in poly(methyl methacrylate).

# Magnesium Ion Selective Two-Photon Fluorescent Probe Based on a Benzo[h]chromene Derivative for in Vivo Imaging\_2007

BF2-Azadipyrromethene dyes are a promising class of NIR emitter (nonhalogenated) and photosensitizer (halogenated). Spectroscopic studies on a benchmark example of each type, including absorption (one and two photon), time-resolved transient absorption (ps–ms) and fluorescence, are reported. Fast photodynamics reveal that intense nanosecond NIR fluorescence is quenched in a brominated analog, giving rise to a persistent (21 μs) transient absorption signature. Kinetics for these changes are determined and ascribed to the efficient population of a triplet state (72%), which can efficiently sensitize singlet oxygen formation (ca. 74%), directly observed by 1Δg luminescence. Photostability measurements reveal extremely high stability, notably for the nonhalogenated variant, which is at least 103-times more stable (Φphotodeg. = < 10–8) than some representative BODIPY and fluorescein dyes.

# Effect of Structural Modifications in the Spectral and Laser Properties of Perylenediimide Derivatives\_2007

Live cell imaging requires bright photostable dyes that can target intracellular organelles and proteins with high specificity in a no-wash protocol. Organic dyes possess the desired photochemical properties and can be covalently linked to various protein tags. The currently available fluorogenic dyes are in the green/yellow range where there is high cellular autofluorescence and the near-infrared (NIR) dyes need to be washed out. Protein-mediated activation of far-red fluorogenic dyes has the potential to address these challenges because the cell-permeant dye is small and nonfluorescent until bound to its activating protein, and this binding is rapid. In this study, three single chain variable fragment (scFv)-derived fluorogen activating proteins (FAPs), which activate far-red emitting fluorogens, were evaluated for targeting, brightness, and photostability in the cytosol, nucleus, mitochondria, peroxisomes, and endoplasmic reticulum with a cell-permeant malachite green analog in cultured mammalian cells. Efficient labeling was achieved within 20–30 min for each protein upon the addition of nM concentrations of dye, producing a signal that colocalized significantly with a linked mCerulean3 (mCer3) fluorescent protein and organelle specific dyes but showed divergent photostability and brightness properties dependent on the FAP. These FAPs and the ester of malachite green dye (MGe) can be used as specific, rapid, and wash-free labels for intracellular sites in live cells with far-red excitation and emission properties, useful in a variety of multicolor experiments.

# BF2-Azadipyrromethenes: Probing the Excited-State Dynamics of a NIR Fluorophore and Photodynamic Therapy Agent\_2011

Carbon nanotube uptake was measured via high-speed confocal Raman imaging in live cells. Spatial and temporal tracking of two cell-intrinsic and nine nanotube-derived Raman bands was conducted simultaneously in RAW 264.7 macrophages. Movies resolved single (n, m) species, defects, and aggregation states of nanotubes transiently as well as the cell position, denoted by lipid and protein signals. This work portends the real-time molecular imaging of live cells and tissues using Raman spectroscopy, affording multiplexing and complete photostability.

# Rapid, Specific, No-wash, Far-red Fluorogen Activation in Subcellular Compartments by Targeted Fluorogen Activating Proteins\_2015

At the forefront of developing fluorescent probes for biological imaging applications are enhancements aimed at increasing their brightness, contrast, and photostability, especially toward demanding applications of single-molecule detection. In comparison with existing probes, nanorubies exhibit unlimited photostability and a long emission lifetime (∼4 ms), which enable continuous imaging at single-particle sensitivity in highly scattering and fluorescent biological specimens. However, their wide application as fluorescence probes has so far been hindered by the absence of facile methods for scaled-up high-volume production and molecularly specific targeting. The present work encompasses the large-scale production of colloidally stable nanoruby particles, the demonstration of their biofunctionality and negligible cytotoxicity, as well as the validation of its use for targeted biomolecular imaging. In addition, optical characteristics of nanorubies are found to be comparable or superior to those of state-of-the-art quantum dots. Protocols of reproducible and robust coupling of functional proteins to the nanoruby surface are also presented. As an example, NeutrAvidin-coupled nanoruby show excellent affinity and specificity to μ-opioid receptors in fixed and live cells, allowing wide-field imaging of G-protein coupled receptors with single-particle sensitivity.

# Measuring Uptake Dynamics of Multiple Identifiable Carbon Nanotube Species via High-Speed Confocal Raman Imaging of Live Cells\_2012

The dependence of single-molecule photoluminescence intermittency (PI) or “blinking” on the local dielectric constant (ε) is examined for nile red (NR) in thin films of poly(vinylidene fluoride) (PVDF). In previous studies, variation of the local dielectric constant was accomplished by studying luminophores in chemically and structurally different hosts. In contrast, the NR/PVDF guest–host pair allows for the investigation of PI as a function of ε while keeping the chemical composition of both the luminophore and host unchanged. The solvatochromic properties of NR are used to measure the local ε, while fluctuations in NR emission intensity over time provide a measure of the PI. PVDF is an ideal host for this study because it provides submicron-sized dielectric domains that vary from nonpolar (ε ≈ 2) to very polar (ε ≈ 70). The results presented here demonstrate that the local dielectric environment can have a pronounced effect on PI. We find that the NR emissive events increase 5-fold with an increase in ε from 2.2 to 74. A complex dependence on ε is also observed for NR nonemissive event durations, initially increasing as ε increases from 2.2 to 3.4 but decreasing in duration with further increase in ε. The variation in emissive event durations with ε is reproduced using a photoinduced electron-transfer model involving electron transfer from NR to PVDF. In addition, an increase in NR photostability with an increase in ε is observed, suggesting that the dielectric environment plays an important role in defining the photostability of NR in PVDF.

# Development of Bright and Biocompatible Nanoruby and Its Application to Background-Free Time-Gated Imaging of G-Protein-Coupled Receptors\_2017

Advances in the development of small photoblinking semiconducting polymer dots (Pdots) have attracted great interest for use in super-resolution microscopy. However, multicolor super-resolution imaging using conventional small photoblinking Pdots remains a challenge due to their limited color choice, broad emission spectrum, and heavy spectrum crosstalk. Here, we introduce two types of small photoblinking Pdots with different colors and relatively narrow emission spectra: blue PFO Pdots and carmine PFTBT5 Pdots for blinking-based statistical nanoscopy. Both of these probes feature ultrahigh single-particle brightness, very strong photostability, superior biocompatibility, and robust fluorescence fluctuation. In addition, these small photoblinking Pdots serve as excellent labels for dual-color super-resolution optical fluctuation imaging (SOFI) of specific subcellular structures, indicating their promise for long-term multicolor SOFI nanoscopy with high spatiotemporal resolution.

# Dielectric Dependence of Single-Molecule Photoluminescence Intermittency: Nile Red in Poly(vinylidene fluoride)\_2014

A highly efficient photoelectrochemical cell was developed using a quantum dot semiconductor coupled hierarchical ZnO nanostructure for hydrogen generation. The hierarchical ZnO nanostructure consists of ZnO nanowire as a core and 2-dimensional ZnO nanosheets shelled on the ZnO nanowire surface. This multi-dimensional nanostructured photoanode was optimized with solution process conditions for efficient charge separation and transportation, and the visible light harvesting was effectively enhanced using the low bandgap semiconductor cadmium chacogenide quantum dots. Our hierarchical ZnO nanowire photoelectrode has greatly improved the saturated photocurrent density (17.5 mA/cm2) at 0.4 V vs. RHE under 1 sun illumination condition. In addition, we have modified the photoelectrode with IrOx·nH2O deposition to enhance the photostability, showing a noticeable improvement in steady generation of photocurrent under the light illumination condition.

# Multicolor Super-resolution Fluorescence Microscopy with Blue and Carmine Small Photoblinking Polymer Dots\_2017

We report a strategy to synthesize highly emissive, photostable, microporous materials by solid-state entrapment of boron dipyrromethene (BODIPY) fluorophores in a metal–organic framework. Solvent-free mechanochemistry or accelerated aging enabled quantitative capture and dispersal of the PM605 dye within the ZIF-8 framework starting from inexpensive, commercial materials. While the design of emissive BODIPY solids is normally challenged by quenching in a densely packed environment, herein reported PM605@ZIF-8 materials show excellent emissive properties and to the best of our knowledge an unprecedented ∼10-fold enhancement of BODIPY photostability. Time-resolved and steady-state fluorescence studies of PM605@ZIF-8 show that interchromophore interactions are minimal at low dye loadings, but at higher ones lead to through-pore energy transfer between chromophores and to aggregate species.

# Highly Efficient Photoelectrochemical Hydrogen Generation Using a Quantum Dot Coupled Hierarchical ZnO Nanowires Array\_2013

Fluorescent carbon dots (CDs) have got tremendous applications in bioimaging, molecular sensing, light harvesting, photovoltaics, catalysis, and drug delivery. This is mainly due to the superior photostability, high quantum yield, aqueous solubility, and low toxicity. However, super resolution nanoscopy using CD has rarely been reported. Here, we report the super-resolution image down to ∼64 nm in the actin filament and in the self-assembled soft matter polymeric ring structure. The photon counts, on–off duty cycles, and the number of switching cycles were good enough to get such a high resolution. This opens up a new door to the realm of application of CD in live-cell nanoscopy.

# Highly Photostable and Fluorescent Microporous Solids Prepared via Solid-State Entrapment of Boron Dipyrromethene Dyes in a Nascent Metal–Organic Framework\_2018

Photostability has been a major issue for perovskite materials. Understanding the photodegradation mechanism and suppressing it are of central importance for applications. By investigating single-dot photoluminescence spectra and the lifetime of MAPbX3 (MA = CH3NH3+, X = Br, I) nanocrystals with quantum confinement under different conditions, we identified two separate pathways in the photodegradation process. The first is the oxygen-assisted light-induced etching process (photochemistry). The second is the light-driven slow charge-trapping process (photophysics), taking place even in oxygen-free environment. We clarified the role of oxygen in the photodegradation process and show how the photoinduced etching can be successfully suppressed by OSTE polymer, preventing an oxygen-assisted reaction.

# Nitrogen-Doped Biocompatible Carbon Dot as a Fluorescent Probe for STORM Nanoscopy\_2018

The effects of fluorophenyl substituents on the photoluminescence, redox properties, and oxygen sensing behaviors of the cyclometalated Pt(II) complexes are reported. The Pt(II) complexes with fluorophenyl substituents at the para position on the phenyl ring of 2-phenylpyridine (ppy) exhibit higher oxygen sensitivities than those at the meta position. Photodegradation tests demonstrate that the introduction of fluorophenyl substituents can strongly improve the photostability of cyclometalated Pt(II) complexes. Fast response and recovery times of oxygen sensing films are obtained in 3.0 s on going from 0% O2 to 100% O2 and in 4.0 s on going from 100% O2 to 0% O2 (95% recovery of the luminescence), respectively. The oxygen sensing films show excellent operational stability in 4000 s saturation O2/N2 cycles, which meets the requirement of monitoring molecular oxygen in real time.

# Photodegradation of Organometal Hybrid Perovskite Nanocrystals: Clarifying the Role of Oxygen by Single-Dot Photoluminescence\_2019

Optical imaging is emerging as an important tool to visualize tumors. However, there are many potential choices among the available fluorophores. Optical imaging probes that emit in the visible range can image superficial tumors with high quantum yields; however, if deeper imaging is needed then near-infrared (NIR) fluorophores are necessary. Most commercially available NIR fluorophores are cyanine based and are prone to nonspecific binding and relatively limited photostability. Silica-containing rhodamine (SiR) fluorophores represent a new class of NIR fluorophores, which permit photoactivation via H-dimer formation as well as demonstrate improved photostability. This permits higher tumor-to-background ratios (TBRs) to be achieved over longer periods of time. Here, we compared an avidin conjugated with SiR700 (Av-SiR700) to similar compounds based on cyanine dyes (Av-Cy5.5 and Av-Alexa Fluor 680) in a mouse tumor model of ovarian cancer metastasis. We found that the Av-SiR700 probe demonstrated superior quenching, enabling activation after binding-internalization to the target cell. As a result, Av-SiR700 had higher TBRs compared to Av-Cy5.5 and better biostability compared to Av-Alexa Fluor 680.

# Photostable Fluorophenyl-Substituted Cyclometalated Platinum(II) Emitters for Monitoring of Molecular Oxygen in Real Time\_2015

The hyperbranched poly(amido amine) nanoparticles (HPAMAM NPs) with multiple functions, such as biodegradability, autofluorescence, and specific affinity, were successfully prepared by Michael addition dispersion polymerization of CBA, AEPZ, and N-galactosamine hydrochloride (or N-glucosamine hydrochloride) in a mixture of methanol/water. The resultant NPs displayed strong photoluminescence, high photostability, broad absorption, and emission (from 430 to 620 nm) spectra. The fluorescence from HPAMAM NPs may be attributed to the tertiary amine chromophore. The incubation results of the liver cancer cells, HepG2, with the NPs showed that the NPs are nontoxic and can be recognized by asialoglycoprotein receptors on the surface of HepG2 and then can be internalized. Therefore, they have potential applications in bioimaging and drug or gene delivery.

# Activatable Optical Imaging with a Silica-Rhodamine Based Near Infrared (SiR700) Fluorophore: A comparison with cyanine based dyes\_2011

Silicon nanoparticles (Si NPs) exhibiting observable luminescence have many electronic, optical, and biological applications. Owing to reduced toxicity, they can be used as cheap and environmentally friendly alternatives for cadmium containing quantum dots, organic dyes, and rare earth-based expensive phosphors. Here, we report an inexpensive silicon precursor, namely rice husk, which has been employed for the synthesis of Si NPs by rapid microwave heating. The Si NPs of ∼4.9 nm diameter exhibit observable green luminescence with a quantum yield of ∼60%. They show robust storage stability and photostability and have constant luminescence during long-term UV irradiation extending over 48 h, in contrast to other luminescent materials such as quantum dots and organic dyes which quenched their emission over this time window. Green luminescent Si NPs upon mixing with synthesized red and blue luminescent Si NP species are shown to be useful for energy-efficient white light production. The resulting white light has a color coordinate of (0.31, 0.27) which is close to that of pure white light (0.33, 0.33). The performance of our white light emitting material is comparable to that of a commercial white light emitting diode (WLED) bulb and is shown to be better than that of a commercial compact fluorescent lamp (CFL).

# Multiple Functional Hyperbranched Poly(amido amine) Nanoparticles: Synthesis and Application in Cell Imaging\_2011

Owing to their potential applications in biomedicine and biotechnology, peptide nanostructures that exhibit stable intrinsic fluorescence in the visible range are highly desired. This research proposes a facile strategy to construct peptidyl virus-like nanoparticles (NVPs) that show green luminescence by coassembly of two bioactive ferrocene-diphenylalanine-based (Fc-FF) peptides. The green fluorescence of NVPs was originated from the highly ordered structures assembled by the amphiphilic Fc-FF-based peptides via strong π–π stacking interactions. In the assemblies, Fc-FF chromophore can be hydrolyzed under the natural light irradiation, which eliminates the fluorophore quenching effect of Fc and increases the aromatic stacking interactions, thereby giving rise to strong fluorescent nanoparticles. The NVPs could cross cytomembrane barriers by virtue of the HIV V3 peptide and the nuclear localization signal, and could thus be used for long-term cell imaging with excellent photostability and biocompatibility in physiological condition. In addition, NVPs could package DNA and be used to monitor the delivery of DNA, indicating great potential in the tracking and monitoring of genetic biological processes.

# Synthesis of Silicon Nanoparticles from Rice Husk and their Use as Sustainable Fluorophores for White Light Emission\_2018

Light-induced degradation of the riboflavin derivatives is reported, including 5-deaza-riboflavin, iso-6,7-riboflavin, 3-methyl-tetra-acetyl-riboflavin (3MeTARF), and 3-benzyl-lumiflavin. The studied compounds undergo photolytic processes with considerable quantum yields in methanolic solutions (φ ≈ 10–3–10–4 mol einst–1). Photolysis in anaerobic conditions is more efficient than that in the presence of oxygen. Experiments show that triplet excited state of flavin molecules is involved in the reactions. The main photoproducts are the respective alloxazinic and isoalloxazinic derivatives of the substrates. 3MeTARF reveals higher photostability than riboflavin. The values of photodegradation quantum yields were estimated for the four studied derivatives.

# Photo- and Aromatic Stacking-Induced Green Emissive Peptidyl Nanoparticles for Cell Imaging and Monitoring of Nucleic Acid Delivery\_2019

We report on the synthesis, structural characterization, physical properties, and lasing action of two organic dyes, Rhodamine 6G (Rh6G) and Pyrromethene 597 (PM597), incorporated into new hybrid organic−inorganic materials, where the organic component was either poly(2-hydroxyethyl-methacrylate) (PHEMA) or copolymers of HEMA with methyl methacrylate (MMA), and the inorganic counterpart consisted of silica derived from hydrolysis−condensation of methyltriethoxysilane (TRIEOS) in weight proportion of up to 30%. Lasing efficiencies of up 23% and high photostabilities, with no sign of degradation in the initial laser output after 100 000 pump pulses at 10 Hz, were demonstrated when pumping the samples transversely at 534 nm with 5.5 mJ/pulse. A direct relationship could be established between the structure of the hybrid materials, analyzed by solid-state NMR, and their laser behavior. An inorganic network dominated by di-/tri- substituted silicates in a proportion ≈35:65, corresponding to samples of HEMA with 15 and 20 wt % proportion of TRIEOS, optimizes the lasing photostability. The thermal properties of these materials, together with the high homogeneity revealed by atomic force microscopy (AFM) images, even in compounds with high silica content, indicate their microstructure to be a continuous phase, corresponding to the polymer matrix, which “traps” the silica components at molecular level via covalent bonding, with few or no silica islands.

# Photochemistry of Riboflavin Derivatives in Methanolic Solutions\_2012

Ultraviolet (UV)-light-induced deactivation (photodenatruation) of enzymes (horseradish peroxidase, HRP) with a limited photostability is drastically inhibited by intercalation into two-dimensional (2D) nanospaces surrounded with semiconducting titanate layers. The enzyme existing in the interlayer can react with substrate molecule through a semiopen structure along the 2D layers even after the incorporation. The UV light is absorbed by the layers with band gaps equivalent to UV regions and then the photodenaturation of bound HRP is retarded in comparison with the native one. It is demonstrated that the optical absorption property of the titanate host layer and the pH-dependent affinity with the guest strongly influence the UV light tolerance of HRP in the interlayer space.

# Synthesis, Structure, and Physical Properties of Hybrid Nanocomposites for Solid-State Dye Lasers\_2005

Here we present a CdS quantum dot sensitized solar cell based on a mesoporous TiO2 film with remarkable stability using I−/I3− electrolyte. Chemical Bath Deposition (CBD) was used to deposit the CdS quantum dots within the porous network. We show that a thin coating of the QD sensitized film with an amorphous TiO2 layer strongly improves the performance and photostability of the solar cell. We propose that the coating passivates QD surface states which act as hole traps and are responsible for photodegradation of the device. In addition, this coating decreases the recombination of electrons from the CdS quantum dots and the mesoporous TiO2 into the electrolyte solution. We obtain a significant improvement of all cell parameters resulting in a total light to electric power conversion efficiency of 1.24%.

# Enhanced Ultraviolet Light Tolerance of Peroxidase Intercalated into Titanate Layers\_2011

We present a detailed CASSCF study of the mechanism of excited-state intramolecular proton transfer (ESIPT) in the o-hydroxyphenyl triazine class of photostabilizers. The valence-bond analysis of the ground state and the two ππ\* excited states permits a simple chemical interpretation of the mechanistic information. Our results show that the barrier to enol−keto tautomerism on the ground-state adiabatic surface is high. Following photoexcitation to the charge-transfer state, the ESIPT is predicted to take place without a barrier. Radiationless decay to the ground state is associated with an extended seam of conical intersection, with a sloped topology lying parallel to the ESIPT path, which can be accessed at any point along the reaction path. Our results show that the triazine class of photostabilizers has the photochemical and photophysical qualities associated with exceptional photostability.

# Core/CdS Quantum Dot/Shell Mesoporous Solar Cells with Improved Stability and Efficiency Using an Amorphous TiO2 Coating\_2009

The increased expression of vascular endothelial growth factor (VEGF) and its receptors is associated with angiogenesis in a growing tumor, presenting potential targets for tumor-selective imaging by way of targeted tracers. Though fluorescent tracers are used for targeted in vivo imaging, the lack of photostability and biocompatibility of many current fluorophores hinder their use in several applications involving long-term, continuous imaging. To address these problems, fluorescent nanodiamonds (FNDs), which exhibit infinite photostability and excellent biocompatibility, were explored as fluorophores in tracers for targeting VEGF receptors in growing tumors. To explore FND utility for imaging tumor VEGF receptors, we used click-chemistry to conjugate multiple copies of an engineered single-chain version of VEGF site-specifically derivatized with trans-cyclooctene (scVEGF-TCO) to 140 nm FND. The resulting targeting conjugates, FND-scVEGF, were then tested for functional activity of the scVEGF moieties through biochemical and tissue culture experiments and for selective tumor uptake in Balb/c mice with induced 4T1 carcinoma. We found that FND-scVEGF conjugates retain high affinity to VEGF receptors in cell culture experiments and observed preferential accumulation of FND-scVEGF in tumors relative to untargeted FND. Microspectroscopy provided unambiguous determination of FND within tissue by way of the unique spectral shape of nitrogen-vacancy induced fluorescence. These results validate and invite the use of targeted FND for diagnostic imaging and encourage further optimization of FND for fluorescence brightness.

# Mechanism of an Exceptional Class of Photostabilizers:  A Seam of Conical Intersection Parallel to Excited State Intramolecular Proton Transfer (ESIPT) in o-Hydroxyphenyl-(1,3,5)-triazine\_2005

A novel ratiometric emission fluorescent probe, 1,1-dimethyl-2-[2-(quinolin-4-yl)vinyl]-1H-benzo[e]indole (QVBI), is facilely synthesized via ethylene bridging of benzoindole and quinoline. The probe exhibits ratiometric fluorescence emission (F522nm/F630nm) characteristics with pKa 3.27 and linear response to extreme-acidity range of 3.8–2.0. Also, its high fluorescence quantum yield (Φ = 0.89) and large Stokes shift (110 nm) are favorable. Moreover, QVBI possesses highly selective response to H+ over metal ions and some bioactive molecules, good photostability, and excellent reversibility. The probe has excellent cell membrane permeability and is further applied successfully to monitor pH fluctuations in live cells and imaging extreme acidity in Escherichia coli cells without influence of autofluorescence and native cellular species in biological systems.

# Targeting Fluorescent Nanodiamonds to Vascular Endothelial Growth Factor Receptors in Tumor\_2019

Water splitting occurring on a semiconductor photocatalyst has become the Holy Grail process to produce a solar fuel, hydrogen, on irradiation with sunlight (or simulated sunlight) in heterogeneous media. Authors often claim highly efficient evolution of hydrogen and oxygen from water through water splitting or efficient hydrogen evolution in the presence of some sacrificial electron donor, whether photocatalytically or photoelectrochemically. Perusal of the scientific and patent literature reveals that yields of hydrogen are disappointingly low even after decades of remarkable advances in materials science and in strategies to achieve significant progress in water splitting. This Review identifies and discusses intrinsic and extrinsic factors (e.g., Φhν = fn{β, kr, S, D, d, s, τ, αhν}; photostability; back reactions) that impact redox reactions in general and water splitting in particular. The lack of control and handling of these various factors present a challenging, if not an impossible task in improving process efficiencies to achieve significant practical evolution of hydrogen from water splitting.

# Ratiometric Emission Fluorescent pH Probe for Imaging of Living Cells in Extreme Acidity\_2015

Copper ions play a crucial role in living systems as cofactors of numerous metalloenzymes. To quantitatively estimate the Cu2+ concentration in human tissue, we have developed a two-photon (TP) probe with an internal reference (ACCu2) that shows significant TP action cross-section and high selectivity for Cu2+ and can quantitatively estimate the Cu2+ concentration in human colon tissues by dual-color two-photon microscopy (TPM) imaging with minimum interference from other competing metal ions or pH and minimum cytotoxicity and photostability problems. The Cu2+ concentrations in human normal colon, polyp, and colon cancer tissues were found to be 8.3 ± 0.3, 13 ± 2, and 22 ± 3 μM, respectively. This result suggests that ACCu2 may be useful for the diagnosis of human colon cancer.

# Why do Hydrogen and Oxygen Yields from Semiconductor-Based Photocatalyzed Water Splitting Remain Disappointingly Low? Intrinsic and Extrinsic Factors Impacting Surface Redox Reactions\_2016

Aryl benzobisoxazole and aryl benzobisthiazole compounds in the solid state and in solution have completely different photoreactivity. In the solid state, intermolecular π-stacking interactions between these molecules lead to excimer formation. The excimer undergoes a photoinduced electron transfer to generate an ion radical pair. In the presence of oxygen, the anion radical transfers an electron to molecular oxygen to form superoxide. The cation radical undergoes bond cleavage followed by hydrogen abstraction and other reactions to form benzobisoxazoles (or benzobisthiazoles), benzonitriles, and benzamides. In solution, aryl benzobisoxazole and aryl benzobisthiazole molecules cannot readily π-stack, and therefore photoinduced electron transfer and its subsequent reactions do not occur. The compounds in solution are stable even after prolonged irradiation, suggesting that intermolecular π-stacking plays a very important role in photoreactivity for these molecules. Reversible redox reagents, such as ferrocene compounds, are found to retard the subsequent reactions from the photoinduced electron-transfer reaction and hence improve the photostability of poly{(benzo[1,2-d:5,4-d‘]bisoxazole-2,6-diyl)-1,4-phenylene}.

# Two-Photon Probe for Cu2+ with an Internal Reference: Quantitative Estimation of Cu2+ in Human Tissues by Two-Photon Microscopy\_2014

Blue luminescent carbon dots (CDs) with a high photoluminescence (PL) quantum yield (48.3 ± 5.3%) were prepared by the one-pot hydrothermal reaction of citric acid with poly(ethylenimine) (PEI). The CDs display bright PL, narrow emission spectra, pH-dependent PL intensity, high photostability, and up-converted luminescence. The CDs exhibit a quenching of both down- and up-conversion PL in the presence of morin and thus serve as useful probes for morin detection. Both down- and up-conversion measurements allow the quantification of concentrations from 0 to 300 μmol/L with a detection limit of 0.6 μmol/L, and this dual-mode detection increases the reliability of the measurement. The proposed method of determination is simple, sensitive, and cost-effective, with potential applications in clinical and biochemical assays.

# Importance of π-Stacking in Photoreactivity of Aryl Benzobisoxazole and Aryl Benzobisthiazole Compounds\_2003

We present a new class of fluorescent carbon dots (CDs) prepared hydrothermally from cationic surfactant cetylpyridinium chloride (CPC). Because of the high carbon content, amphiphilicity, and the presence of a heteroaromatic π system, CPC acts as a carbon source, stabilizing agent, and contributing fluorophore in the prepared CDs-based system. The surfactant-derived carbon dots exhibit amphiphilicity, tunable blue–green–yellow photoluminescence dependent upon the solvent polarity, reaction conditions, and excitation wavelength, excellent long-term colloidal and photostability, and a large-scale synthesis potential. The reported findings open the doors for the applicability of surfactants as a carbon source for nanosystems with controllable photoluminescence and amphiphilicity.

# One-Pot Hydrothermal Synthesis of Carbon Dots with Efficient Up- and Down-Converted Photoluminescence for the Sensitive Detection of Morin in a Dual-Readout Assay\_2017

The iridium(III)–cyanine complex (IrCy) was fabricated by conjugating an iridium(III) complex to a cyanine dye with an intense near-infrared (NIR) absorption. IrCy complex nanoparticles (NPs) with high water solubility and photostability were prepared by a solvent evaporation-induced self-assembly strategy. Considering their effective photacoustic (PA) imaging and generation of 1O2 property with 808 nm laser irradiation in aqueous solution, PA imaging guided NIR-driven photodynamic therapy in vivo was effectively conducted in the 4T1 xenograft model. We developed a real-time PA imaging methodology to investigate the pharmacokinetics, tumor targeting, and biodistribution of IrCy NPs. Taking advantage of the analysis of the PA signal of the common iliac vein, the blood circulation half-life of IrCy NPs in mice was calculated to be ∼18 h, and the enhanced permeability and retention effect of IrCy NPs offered the maximum targeting property in the tumor at about 24 h. The obvious change of PA imaging signal in kidney and bladder confirmed IrCy NPs should be excreted partially from the urine system, and the PA signal decreased from 12.5× to 2.8× in the liver, and from 28.8× to 9.4× in the spleen also confirmed the hepatic metabolic pathway.

# Surfactant-Derived Amphiphilic Carbon Dots with Tunable Photoluminescence\_2013

Nonlinear optical nanocrystals have been recently introduced as a promising alternative to fluorescent probes for multiphoton microscopy. We present for the first time a complete survey of the properties of five nanomaterials (KNbO3, LiNbO3, BaTiO3, KTP, and ZnO), describing their preparation and stabilization and providing quantitative estimations of their nonlinear optical response. In the light of their prospective use as biological and clinical markers, we assess their biocompatibility on human healthy and cancerous cell lines. Finally, we demonstrate the great potential for cell imaging of these inherently nonlinear probes in terms of optical contrast, wavelength flexibility, and signal photostability.

# Photostable Iridium(III)–Cyanine Complex Nanoparticles for Photoacoustic Imaging Guided Near-Infrared Photodynamic Therapy in Vivo\_2019

Phototherapy of cancer attracted a great deal of attention in recent years, and novel eligible photothermal agent (PTA) with good photostability and excellent photothermal effect is highly needed. Herein, Fe3+-doped poly(2-nitro-1,4-phenylenediamine) hollow spheres were successfully prepared at room temperature via a simple solution-based wet chemical synthesis method. The resultant products exhibited excellent biocompatibility and good photothermal effect. The in vitro and in vivo evaluation demonstrates good cancer cell killing effect and the excellent antitumor efficacy of Fe3+-doped poly(2-nitro-1,4-Phenylenediamine) via photothermal therapy (PTT) for the first time.

# Harmonic Nanocrystals for Biolabeling: A Survey of Optical Properties and Biocompatibility\_2012

Biomedicine and cell and molecular biology require powerful imaging techniques of the single molecule scale to the whole organism, either for fundamental science or diagnosis. These applications are however often limited by the optical properties of the available probes. Moreover, in cell biology, the measurement of the cell response with spatial and temporal resolution is a central instrumental problem. This has been one of the main motivations for the development of new probes and imaging techniques either for biomolecule labeling or detection of an intracellular signaling species. The weak photostability of genetically encoded probes or organic dyes has motivated the interest for different types of nanoparticles for imaging such as quantum dots, nanodiamonds, dye-doped silica particles, or metallic nanoparticles. One of the most active fields of research in the past decade has thus been the development of rare-earth based nanoparticles, whose optical properties and low cytotoxicity are promising for biological applications. Attractive properties of rare-earth based nanoparticles include high photostability, absence of blinking, extremely narrow emission lines, large Stokes shifts, long lifetimes that can be exploited for retarded detection schemes, and facile functionalization strategies. The use of specific ions in their compositions can be moreover exploited for oxidant detection or for implementing potent contrast agents for magnetic resonance imaging. In this review, we present these different applications of rare-earth nanoparticles for biomolecule detection and imaging in vitro, in living cells or in small animals. We highlight how chemical composition tuning and surface functionalization lead to specific properties, which can be used for different imaging modalities. We discuss their performances for imaging in comparison with other probes and to what extent they could constitute a central tool in the future of molecular and cell biology.

# Ion-Doped Poly(2-Nitro-1,4-Phenylenediamine) Hollow Nanospheres for Photothermal Therapy\_2019

We reported a ratiometric two-photon fluorescent probe (SG1) for β-galactosidase (β-gal) and its application to quantitative detection of β-gal activity during cellular senescence in live cells and in aged tissues. This probe is characterized by a significant two-photon excited fluorescence, a marked blue-to-yellow emission color change in response to β-gal, easy loading, insensitivity to pH and reactive oxygen species (ROS), high photostability, and low cytotoxicity. In addition, we show that SG1 labeling is an effective tool for quantitative detection of senescence-associated β-gal activity at the subcellular level in situ. This finding demonstrates that SG1 will find useful applications in biomedical research, including studies of cell aging.

# Biological Applications of Rare-Earth Based Nanoparticles\_2011

The century-old fluoresceins and rhodamines persist as flexible scaffolds for fluorescent and fluorogenic compounds. Extensive exploration of these xanthene dyes has yielded general structure–activity relationships where the development of new probes is limited only by imagination and organic chemistry. In particular, replacement of the xanthene oxygen with silicon has resulted in new red-shifted Si-fluoresceins and Si-rhodamines, whose high brightness and photostability enable advanced imaging experiments. Nevertheless, efforts to tune the chemical and spectral properties of these dyes have been hindered by difficult synthetic routes. Here, we report a general strategy for the efficient preparation of Si-fluoresceins and Si-rhodamines from readily synthesized bis(2-bromophenyl)silane intermediates. These dibromides undergo metal/bromide exchange to give bis-aryllithium or bis(aryl Grignard) intermediates, which can then add to anhydride or ester electrophiles to afford a variety of Si-xanthenes. This strategy enabled efficient (3–5 step) syntheses of known and novel Si-fluoresceins, Si-rhodamines, and related dye structures. In particular, we discovered that previously inaccessible tetrafluorination of the bottom aryl ring of the Si-rhodamines resulted in dyes with improved visible absorbance in solution, and a convenient derivatization through fluoride-thiol substitution. This modular, divergent synthetic method will expand the palette of accessible xanthenoid dyes across the visible spectrum, thereby pushing further the frontiers of biological imaging.

# Ratiometric Two-Photon Fluorescent Probe for Quantitative Detection of β-Galactosidase Activity in Senescent Cells\_2014

Urea is a small molecule produced in millions of tons per day and is ubiquitous in nature. Biological treatment is commonly used to oxidize the urea wastewater produced each day across the world, which produces additional solid waste and eliminates any potential for utilizing the stored chemical energy within. A solar waste-to-fuels concept is presented to synergistically produce hydrogen fuel from visible sunlight while remediating urea wastewaters. A cascade semiconductor-catalyst electrode assembly was designed to drive the photoconversion of urea to hydrogen. Proper band energy alignment facilitates catalyst activation via hole transfer across the semiconductor–catalyst interface. Specifically CdS-sensitized TiO2 with Ni(OH)2 urea electrocatalyst on fluorine-doped tin oxide coated glass was employed as photoanode. The steady-state response of the semiconductor–catalyst electrode is investigated in a photoelectrochemical cell, and charge transfer and recombination kinetics are elucidated to identify limiting charge-transfer reactions within the electrode architecture. Back electron transfer from semiconductor to catalyst is found to be competitive with urea oxidation reaction, which hinders steady-state photoconversion efficiency. Furthermore, the photoanode rapidly decomposes in urea electrolyte solutions as a result of the water-mediated photocorrosion of chalcogenide electrodes. Passivation of CdS with ZnS prior to catalyst deposition significantly improves open-circuit potential and photostability.

# General Synthetic Method for Si-Fluoresceins and Si-Rhodamines\_2017

Silica encapsulated perylenediimide (PDI) nanoellipsoids with core–shell structure have been synthesized in solution by a combination of precipitation method and sol–gel chemistry. Electron energy loss spectrum (EELS) analysis proves that the obtained composite particles consist of a PDI core and a silica shell. The UV–vis and fluorescence spectra show the strong π–π stacking state of PDI molecules in the composite colloids. The silica deposition process on the PDI surface can be well controlled allowing variation of the shell thickness from 10 to 50 nm. Thermogravimetrical analysis data indicate that the thermal stability of PDI increases after deposition of a silica shell. The photostability of PDI is enhanced by the introduction of silica shell. The silica coating improves the dispersibility of PDI in different solvents and in polymer films.

# Ni(OH)2 as Hole Mediator for Visible Light-Induced Urea Splitting\_2018

We report a general approach to light-emitting polymer nanofibers (PNFs) based on waveguiding excitation. By waveguiding excitation light along the PNFs, we demonstrated that the interaction of light with PNFs is enhanced over 3 orders of magnitude compared with the currently used irradiating excitation. Intriguing advantages such as enhanced excitation efficiency, low excitation power operation down to nW levels, tightly confined excitation with low cross talk, and high photostability of the light-emitting PNFs are obtained. The waveguiding excitation allows incorporation of various fluorescent dyes into PNFs to generate multicolor emitting sources covering the entire visible spectrum. The light-emitting single PNFs via waveguiding excitation may find widespread nanophotonic applications in chemical and biological sensors, multicolor emitting sources, and lasers.

# Synthesis of Silica Encapsulated Perylenetetracarboxylic Diimide Core–Shell Nanoellipsoids\_2011

Organic solar cells (OSC) based on low-band-gap thienothiophene–benzodithiophene copolymer have achieved relatively high efficiency (7–9%) in recent times. Among this class of material, poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB-7) is one of the high-efficiency materials reported for OSC. However, this material seems to be intrinsically unstable compared to the commonly used workhorse polymer, poly(3-hexylthiophene) (P3HT), especially when illuminated in air. Inverted device architecture is usually adopted to improve device stability, but the device stability using PTB-7 is not yet well-understood. In this work, a systematic degradation study on a PTB-7:PC71BM-based inverted OSC employing F-TiOx as electron-transport layer (ETL) was conducted for the first time. Air stability, photostability in inert atmosphere, and photostability under ambient conditions of the device were separately carried out to understand better the polymer behavior in inverted OSC. The device’s air stability with different polymer absorber layers was studied by exposing the devices in air for up to 1500 h. Because of the long and easily cleavable alkoxy side chains in the polymer backbone, a PTB-7:PC71BM-based inverted OSC device is highly susceptible to oxygen and moisture when compared to a P3HT:PC61BM-based device. In addition, with the presence of F-TiOx ETL, a significant reduction in light-soaking time was also observed in PTB-7:PC71BM inverted OSC for the first time. The TiOx/organic interface was found to be responsible for the reduction in the light-soaking time.

# Light-Emitting Polymer Single Nanofibers via Waveguiding Excitation\_2010

Rhodamine B-doped poly(3-mercaptopropylsilsesquioxane) (RB-PMPSQ) fluorescent microspheres with thiol groups were prepared by a facile sol–gel method. Initially, 3-mercaptopropyltrimethoxysilane (MPTMS) monomer was hydrolyzed in an aqueous acid solution with rhodamine B (RB) as the hydrolysis catalyst and the fluorescent dye at the same time, and then an ammonia solution was added into the reaction solution to catalyze the condensation reactions of silanol. Through this method, a high yield of RB-PMPSQ fluorescent microspheres with narrow distribution of particle sizes was obtained, and the size of the particles could be effectively controlled depending upon the concentration of the monomer. The morphology and the fluorescent property of RB-PMPSQ microspheres were characterized by scanning electron microscopy (SEM) and fluorescence spectrophotometer, respectively. The fluorescent microspheres showed excellent photostability. The formation mechanism of the fluorescent microspheres was also proposed.

# Device Stability and Light-Soaking Characteristics of High-Efficiency Benzodithiophene–Thienothiophene Copolymer-Based Inverted Organic Solar Cells with F-TiOx Electron-Transport Layer\_2015

Photothermal nanodrugs based on biomolecules are critically important for advancing photothermal therapy (PTT). However, constructing photothermal nanodrugs from biomolecules is highly challenging because most biomolecules are inherently nonpigmented. Herein, we synthesize well-defined, uniform photothermal nanodrugs through a covalent assembly approach by using nonpigmented peptides and iridoids as building blocks. The resulting photothermal nanodrugs show broad absorption from the UV to the near-infrared (NIR) region, high photothermal conversion efficiency along with robust photostability, and selective tumor accumulation, leading to highly efficient tumor ablation via PTT. This work represents the first example of photothermal nanodrugs that can be constructed by using nonpigmented biomolecules as building blocks and thus will conceivably promote the preclinical evaluation and clinical translation of PTT.

# Facile Synthesis of Rhodamine B-Doped Poly(3-mercaptopropylsilsesquioxane) Fluorescent Microspheres with Controllable Size\_2013

The emissive properties of both doped and nondoped graphene quantum dots (GQDs) with sizes ranging from 3 to 11 nm were analyzed at the single particle level. Both doped and nondoped GQDs are a composite of particles exhibiting green, red, or NIR fluorescence on excitation at 488, 561, and 640 nm, respectively. Nitrogen-doped GQDs (N-GQDs) with diameters ranging from 3.4 to 5.2 nm show a larger proportion of particles with NIR emission as compared to nondoped particles. Doping of GQDs also resulted in changes in the photostability and the fluorescence intermittency seen in single GQD particles. While milliseconds to seconds time scale blinking was regularly observed for red-emitting nondoped GQDs, nitrogen doping significantly reduced blinking. Both doped and nondoped particles also exhibit moderate size dependent photophysical properties.

# Robust Photothermal Nanodrugs Based on Covalent Assembly of Nonpigmented Biomolecules for Antitumor Therapy\_2019

Multilayers of nanoburger structures of silver island films−SiO2−silver island films (SIFs−SiO2−SIFs) were used as substrates to study the fluorescence of close-proximity fluorophores. Compared to single-layered SIFs, multilayer nanoburgers exhibit several distinctive properties including a significantly enhanced fluorescence intensity, decreased lifetimes, and increased fluorphore photostability by simply varying the dielectric layer thickness while the SIF layer is kept constant. Finite-difference time-domain (FDTD) calculations show that the maximum electric field intensity can be tuned by varying the distance between the silver particles. Enhanced fluorescence emission coupled with a reduced fluorophore lifetime suggests that both an electric field and plasmon-coupling component are the underlying mechanisms for nanoburger-based metal-enhanced fluorescence (MEF). This tunable multilayer nanoburger structure holds great potential for applications in biology, microscopy, imaging, and biomedical research, given the current uses of MEF.

# Size and Dopant Dependent Single Particle Fluorescence Properties of Graphene Quantum Dots\_2015

Fluorescent organic dots are emerging as promising bioimaging reagents because of their high brightness, good photostability, excellent biocompatibility, and facile surface functionalization. Organic dots with large two-photon absorption (TPA) cross sections are highly desired for two-photon fluorescence microscopy. In this work, we report two biocompatible and photostable organic dots fabricated by encapsulating tetraphenylethene derivatives within DSPE-PEG matrix. The two organic dots show absorption maxima at 425 and 483 nm and emit green and red fluorescence at 560 and 645 nm, with high fluorescence quantum yields of 64% and 22%, respectively. Both organic dots exhibit excellent TPA property in the range of 800–960 nm, affording upon excitation at 820 nm remarkably large TPA cross sections of 1.2 × 106 and 2.5 × 106 GM on the basis of dot concentration. The bare fluorophores and their organic dots are biocompatible and have been used to stain living cells for one- and two-photon fluorescence bioimagings. The cRGD-modified organic dots can selectively target integrin αvβ3 overexpressing breast cancer cells for targeted imaging. The organic dots are also applied for real-time two-photon fluorescence in vivo visualization of the blood vasculature of mouse ear, providing the spatiotemporal information about the whole blood vascular network. These results demonstrate that the present fluorescent organic dots are promising candidates for living cell and tissue imaging.

# Metal-Enhanced Fluorescence from Silver−SiO2−Silver Nanoburger Structures\_2010

Aggregation-induced emission (AIE) is a fast-developing hot research area in recently years. AIE materials are fascinating because of their efficient aggregated state emission, strong photostability, structural and property diversity, etc. Besides the classical AIE luminogens such as tetraphenylethene and hexaphenylsilole, new AIE structural motifs have been updated rapidly. In this chapter, the development of AIE structural motifs in the past two years will be introduced with the emphasis on the structural design, the mechanistic understanding, and the luminescence behavior of new AIE systems.

# Biocompatible Green and Red Fluorescent Organic Dots with Remarkably Large Two-Photon Action Cross Sections for Targeted Cellular Imaging and Real-Time Intravital Blood Vascular Visualization\_2015

A high brightness red fluorescent probe (S-BODIPY) has been developed for the sensitive and specific imaging of HClO/ClO– in vitro and in vivo. This probe exhibits some distinctive features such as excellent resistance to photobleaching, a high fluorescence brightness, high selectivity, as well as a good biocompatibility. Upon oxidation of the thio-ether group into sulfoxide, the probe showed a noticeable ratiometric fluorescence response toward ClO– with fast response (within 30 s) and a low detection limit (59 nM). The probe demonstrated the successful imaging of exogenous and endogenous HClO/ClO– in living HeLa cells, zebrafish, and mice with high signal-to-noise ratios. S-BODIPY allows for the real-time monitoring the level of ClO– in living cells by ratiometric fluorescence imaging, opening up exciting prospects to develop red and even near-infrared BODIPYs with high brightness and good photostability for in vivo imaging.

# Recent Progress in New AIE Structural Motifs\_2016

This paper reports the molecularly imprinted polymer (MIP)-based fluorescence nanosensor which is developed by anchoring the MIP layer on the surface of silica nanospheres embedded CdSe quantum dots (QDs) via a surface molecular imprinting process. The molecularly imprinted silica nanospheres (CdSe@SiO2@MIP) were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), IR spectroscopy, and so forth, which demonstrated the formation of uniform core−shell lambda-cyhalothrin(LC)-imprinted silica nanospheres. The synthesized CdSe@SiO2@MIP shows higher photostability, and allows a highly selective and sensitive determination of LC via FL intensity decreasing when removal of the original templates. The CdSe@SiO2@MIP was applied to detect trace LC in water without the interference of other pyrethroids and ions. Under optimal conditions, the relative FL intensity of CdSe@SiO2@MIP decreased linearly with the increasing LC in the concentration in the range of 0.1−1000 μM with a detection limit (3σ) of 3.6 μg·L−1. It is found that LC can quench the luminescence of CdSe@SiO2@MIP in a concentration-dependent manner that is best described by a Stern−Volmer-type equation. The possible mechanism is discussed.

# In Vivo Imaging of Endogenously Produced HClO in Zebrafish and Mice Using a Bright, Photostable Ratiometric Fluorescent Probe\_2019

Many aspects of cell metabolism are controlled by acidic pH. We report a new family of small molecule and ratiometric two photon (TP) probes derived from benzimidazole (BH1–3 and BH1L) for monitoring acidic pH values. These probes are characterized by a strong two-photon excited fluorescence, a marked blue-to-green emission color change in response to pH, pKa values ranging from 4.9 to 6.1, a distinctive isoemissive point, negligible cytotoxicity, and high photostability, thereby allowing quantitative analysis of acidic pH. Moreover, we show that BH1L optimized as a lysosomal-targeted probe allows for direct, real-time estimation of the pH values inside lysosomal compartments in live cells as well as in living mouse brain tissues through the use of two-photon microscopy. These findings demonstrate that these probes will find useful applications in biomedical research.

# Molecularly Imprinted Silica Nanospheres Embedded CdSe Quantum Dots for Highly Selective and Sensitive Optosensing of Pyrethroids\_2010

Silver nanoclusters (AgNCs) were first coated with bovine serum albumin (BSA) and then encapsulated into porous metal–organic frameworks of ZIF-8 by the protein-mediated biomineralization process. Unexpectedly, the fluorescence intensities of the yielded AgNCs-BSA@ZIF-8 nanocomposites were discovered to be continuously enhanced during each of the BSA coating and ZIF-8 encapsulation steps. Compared to common AgNCs, greatly improved photostability and storage stability of AgNCs could also be expected. More importantly, having benefited from the ZIF-8 shells, the prepared nanocomposites could possess the specific accumulation and sensitive response to Cu2+ ions, resulting in the rational quenching of their fluorescence intensities. Moreover, AgNCs-BSA@ZIF-8 nanocomposites were coated onto the hydrophobic arraying slides toward a microdots array-based fluorimetric method for the fast and sensitive evaluation of Cu2+ ions. It was discovered that the developed fluorimetric strategy could ensure the high-throughput analysis of Cu2+ ions in wide pH range, and especially some harsh and high-salt media. It can allow for the detection of Cu2+ ions in blood with the concentrations ranging from 4.0 × 10–4 to 160 μM, thus serving as a new copper detection candidate to be widely applied in clinical test, food safety, and environmental monitoring fields.

# Benzimidazole-Based Ratiometric Two-Photon Fluorescent Probes for Acidic pH in Live Cells and Tissues\_2013

Fluorescence indicator/layered double hydroxide (LDH) ultrathin films (UTFs) have been fabricated by alternate assembly of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) and Zn–Al LDH nanosheets on quartz substrates using the layer-by-layer (LBL) deposition technique and demonstrated to be good fluorescence chemosensors for Cd2+. The stepwise and regular growth of the ABTS/LDH UTFs with increasing deposition cycle was monitored by UV–vis absorption and fluorescence emission spectroscopy; a periodic layered structure perpendicular to the substrates with a thickness of 2.40–2.58 nm per bilayer was observed by X-ray diffraction, atomic force microscopy, and scanning electron microscopy. The fluorescence anisotropy of the UTFs was also observed by the polarization fluorescence technique. In addition, a fluorescence chemosensory UTF (20 bilayers) for Cd2+ exhibited a low detection limit (9.5 nM), good repeatability (relative standard deviation less than 3% in 20 consecutive measurements), high photostability and storage stability (with ∼94.1% of the initial fluorescence intensity remaining after 1 month), and excellent selectivity toward Cd2+ from Zn2+ in the physiological pH range (6.5–7.5). The regeneration of the fluorescence chemosensor can be achieved by the use of ethylenediamine tetraacetic acid (EDTA). The mechanism is based on the competitive complexation of Cd2+ between EDTA in solution and ABTS in the UTF, as confirmed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and fluorescence anisotropy measurements. Therefore, this work provides a facile approach for the fabrication of chemosensors based on the incorporation of a fluorescence indicator into an inorganic two-dimensional matrix that can potentially be applied for the detection and measurement of Cd2+.

# Silver Nanoclusters Encapsulated into Metal–Organic Frameworks with Enhanced Fluorescence and Specific Ion Accumulation toward the Microdot Array-Based Fluorimetric Analysis of Copper in Blood\_2018

A novel hydrophilic fluorescence temperature probe (PNDP) based on polarity-sensitive triarylboron compound (DPTB) and PNIPAM is designed and synthesized. In order to overcome the shortcomings of the single-intensity-based sensing mechanism and obtain more robust signals, ratiometric readout is achieved by designing an efficient FRET system (PNDP-NR) between DPTB and Nile Red (NR). PNDP-NR possesses some excellent features, including wide temperature range, good linear relationship, high temperature resolution, excellent reversibility, and stability. Within a sensing temperature range of 30–55 °C, the fluorescence color of PNDP-NR experiences significant change from red to green-blue. PNDP-NR is also introduced into NIH/3T3 cells to sense the temperature at the single-cell level. It gave excellent photostability and low cytotoxicity in vivo.

# Fluorescence Chemosensory Ultrathin Films for Cd2+ Based on the Assembly of Benzothiazole and Layered Double Hydroxide\_2011

Fluorescent probes are essential for the exploration of protein function, detection of molecular interactions, and conformational changes. The nitrilotriacetic acid derivatives of different chromophores were successfully used for site-selective noncovalent fluorescence labeling of histidine-tagged proteins. All of them, however, suffer from the same drawback—loss of the fluorescence upon binding of the nickel ions. Herein we present the solution and solid phase synthesis of water-soluble perylene(dicarboximide) functionalized with a nitrilotriacetic acid moiety (PDI-NTA). The photophysical properties of PDI-NTA revealed an exceptional photostability and fluorescence quantum yield that remained unchanged upon addition of nickel ions. The F1 complex of F0F1-ATP synthase from Escherichia coli, containing three hexahistidine tags, was labeled and the suitability for site-specific labeling of the new chromophore demonstrated using fluorescence correlation spectroscopy.

# Intracellular Fluorescent Temperature Probe Based on Triarylboron Substituted Poly N-Isopropylacrylamide and Energy Transfer\_2015

Probiotics has attracted great attention in food nutrition and safety research field, but thus far there are limited analytical techniques for visualized and real-time monitoring of the probiotics when they are ingested in vivo. Herein, the optical bioimaging technique has been introduced for investigation of foodborne probiotics biodistribution in vivo, employing the near-infrared (NIR) emitting persistent luminescence nanophosphors (PLNPs) of Cr3+-doped zinc gallogermanate (ZGGO) as the contrast nanoprobes. The ultrabrightness, super long afterglow, polydispersed size, low toxicity, and excellent photostability and biocompatibility of PLNPs were demonstrated to be qualified as a tracer for labeling probiotics via antibody (anti-Gram positive bacteria LTA antibody) recognition as well as contrast agent for long-term bioimaging the probiotics. In vivo optical bioimaging assay showed that the LTA antibody functionalized ZGGO nanoprobes that could be efficiently tagged to the probiobics were successfully applied for real-time monitoring and nondamaged probing of the biodistribution of probiotics inside the living body after oral administration. This work presents a proof-of-concept that exploited the bioimaging methodology for real-time and nondamaged researching the foodborne probiotics behaviors in vivo, which would open up a novel way of food safety detection and nutrition investigation.

# Exploiting the Nitrilotriacetic Acid Moiety for Biolabeling with Ultrastable Perylene Dyes\_2008

A straightforward and simpler use of an age-old technique was utilized for the fabrication of “red-emitting magnesium-nitrogen-embedded carbon dots” (r-Mg-N-CD) from the leaves extract of Bougainvillea plant as a natural source of carbon. This technique is similar to the solvent-based technique, which is used for the extraction of fragrances and essential oils from flowers and leaves. The as-derived leaves extract was further carbonized using a simple domestic microwave to obtain the small-sized red-emitting carbonaceous material as r-Mg-N-CD. The r-Mg-N-CD showed excitation-independent emissions at ∼678 nm with excellent photostability and a high quantum yield value (∼40%). Moreover, the important perspective of the present finding is to use this r-Mg-N-CD as a potential photocatalyst material for the degradation of pollutant dye (methylene blue) under the presence of sunlight. To infer the significant influence of using natural sunlight in the process of dye degradation, a comparative analysis was performed, demonstrating the higher rate of photodegradation (∼6 times faster) under the influence of sunlight compared to the artificial visible-light from a 100 W tungsten bulb.

# Persistent Luminescence Nanophosphor Involved Near-Infrared Optical Bioimaging for Investigation of Foodborne Probiotics Biodistribution in Vivo: A Proof-of-Concept Study\_2017

PbSe/CdSe core/shell quantum dots (QDs) were prepared and investigated as thick films using temperature-dependent photoluminescence. In addition to increased photostability, the CdSe shell leads to a four-fold increase of the activation energy for nonradiative exciton decay for the core/shell QDs compared to that for the bare PbSe QDs. The onset for exponential decay of luminescence is ∼240 K in the core/shell samples. From further analysis of the temperature-dependent photoluminescence shift and emission line width, we find that the cation exchange reaction broadens the QD size distribution and increases the temperature-independent state broadening. However, the temperature-dependent contribution to the line shape of the core/shell QDs is similar to that in the cores.

# Sunlight-Induced Photocatalytic Degradation of Pollutant Dye by Highly Fluorescent Red-Emitting Mg-N-Embedded Carbon Dots\_2018

Accurate measurements of intracellular pH are of crucial importance in understanding the cellular activities and in the development of intracellular drug delivery systems. Here we report a highly sensitive pH probe based on a fluorescein-conjugated Au22 nanocluster. Steady-state photoluminescence (PL) measurements have shown that, when conjugated to Au22, fluorescein exhibits more than 160-fold pH-contrasting PL in the pH range of 4.3–7.8. Transient absorption measurements show that there are two competing ultrafast processes in the fluorescein-conjugated Au22 nanocluster: the intracore-state relaxation and the energy transfer from the nonthermalized states of Au22 to fluorescein. The latter becomes predominant at a higher pH, leading to dramatic PL enhancement of fluorescein. In addition to the intrinsically low toxicity, fluorescein-conjugated Au22 nanoclusters exhibit high pH sensitivity, wide dynamic range, and excellent photostability, providing a powerful tool for the study of intracellular processes.

# Four-Fold Enhancement of the Activation Energy for Nonradiative Decay of Excitons in PbSe/CdSe Core/Shell versus PbSe Colloidal Quantum Dots\_2010

We have developed a novel aromatic fluorine-induced one-pot synthesis of ring-perfluorinated trimethine cyanine dye without the use of a pyridine by reacting hexafluorobenzoindolenine with 5 equiv of methyl trifluoromethanesulfonate in mixed solvents of dimethylformamide and toluene. The thus-obtained ring-perfluorinated trimethine cyanine dye shows much better fluorescence properties, including intensity, quantum yield, and lifetime, than the nonfluorinated dye, not only in CH2Cl2 solution and the poly(methyl methacrylate) film but also in the powder state. Furthermore, ring-perfluorinated trimethine cyanine dye 2a shows better photostability toward white light-emitting diode irradiation than nonfluorinated dye trimethine cyanine dye 2b.

# Unique Energy Transfer in Fluorescein-Conjugated Au22 Nanoclusters Leading to 160-Fold pH-Contrasting Photoluminescence\_2018

Graphene quantum dots (GQDs) are emerging fluorescence reporters attractive for optical sensing, owing to their high photostability, highly tunable photoluminescence, molecular size, atomically thin structure, biocompatibility, and ease of functionalization. Herein, we present a fluorometric sensing platform based on tyramine-functionalized GQDs, which is able to detect a spectrum of metabolites with high sensitivity and specificity. Furthermore, multiparametric blood analysis (glucose, cholesterol, l-lactate, and xanthine) is demonstrated. This convenient metabolite profiling technique could be instrumental for diagnosis, study, and management of metabolic disorders and associated diseases, such as diabetes, obesity, lactic acidosis, gout, and hypertension.

# Aromatic Fluorine-Induced One-Pot Synthesis of Ring-Perfluorinated Trimethine Cyanine Dye and Its Remarkable Fluorescence Properties\_2019

We report the synthesis and photochemical behavior of five photochromic molecular switches 7a–e with attached molecular wires based on differently substituted oligo(phenylene ethynylene) (OPE) building blocks. The switchable molecular wires 7a–e were built in a convergent approach from substituted iodotolans 6a–e and 1,2-bis(2-methyl-5-ethynylfuran-3-yl)perfluorocyclopentene 5 by 2-fold Sonogashira coupling. Compound 5 was prepared from the corresponding bis-aldehyde 2 by Wittig-type olefination with [PPh3CHBr2]Br·CH3CN, followed by elimination to the bromoalkyne under mild phase-transfer conditions at 0 °C. Halogen–metal exchange with i-PrMgCl·LiCl and hydrolysis furnished 5 in good overall yield. Substituents R1 and R2 in the OPE portion were either electron-withdrawing or electron-donating, and their influence on the photostability and photoswitching characteristics of 7a–e was studied. All resulting molecules show reversible photochromism between the colorless off and the deeply colored on states when irradiated with light of 313 and 576 nm wavelengths, respectively. The quantum yields of these photoreactions increased when electron-withdrawing groups were used. This was further corroborated by reversible protonation/deprotonation of 7e (R1 = NMe2, R2 = H) for which the ring-closing quantum yield increased 10-fold upon switching off the donor by protonation.

# Ultrasensitive Profiling of Metabolites Using Tyramine-Functionalized Graphene Quantum Dots\_2016

To address the concern of material chemists over the issue of stability and photoluminescent (PL) characteristics of Cu nanoclusters (NCs), herein we present an efficient protocol discussing PL Cu NCs (Cu/HSA) having blue emission and high photostability. These PL NCs were illustrated as efficient probes for Förster resonance energy transfer (FRET) with a compatible fluorophore (Coumarin 153). Our spectroscopic results were well complemented by our molecular docking calculations, which also favored our proposed mechanism for Cu NC formation. The beneficial aspect and uniqueness of these nontoxic Cu/HSA NCs highlights their temperature-dependent PL reversibility as well as the reversible FRET with Coumarin 153, which enables them to be used as a nanothermometer and a PL marker for sensitive biological samples.

# Synthesis and Photoswitching Studies of OPE-Embedded Difurylperfluorocyclopentenes\_2013

We report the solvatochromic, viscosity-sensitive, and single-molecule photophysics of the fluorophores DCDHF-N-6 and DCDHF-A-6. These molecules are members of the dicyanomethylenedihydrofuran (DCDHF) class of single-molecule emitters that contain an amine electron donor and a DCDHF acceptor linked by a conjugated unit; DCDHF-N-6 and DCDHF-A-6 have naphthalene- and anthracene-conjugated linkers, respectively. These molecules maintain the beneficial photophysics of the phenylene-linked DCDHF (i.e., photostability, emission wavelength dependence on solvent polarity, and quantum yield sensitivity to solvent viscosity), yet offer absorption and emission at longer wavelengths that are more appropriate for cellular imaging. We demonstrate that these new fluorophores are less photolabile in an aqueous environment than several other commonly used dyes (rhodamine 6G, Texas Red, and fluorescein). Finally, we image single copies of the acene DCDHFs diffusing in the plasma membrane of living cells.

# Photostable Copper Nanoclusters: Compatible Förster Resonance Energy-Transfer Assays and a Nanothermometer\_2015

A single step facile synthesis of highly emissive, water-soluble, fluorescent Ag nanoclusters has been reported using a small molecule, dihydrolipoic acid. These clusters were characterized using ultraviolet/visible (UV/vis) spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy (FT-IR), high-resolution transmission electron microscopy (HR-TEM), dynamic light scattering (DLS), and X-ray diffraction (XRD) studies. Mass spectrometric analysis shows the presence of a few atoms in nanoclusters containing only Ag4 and Ag5. The reported fluorescent Ag nanoclusters show excellent optical properties, including narrow emission profile, larger Stokes shift (more than 200 nm), and good photostability. Interestingly, these nanoclusters also exhibit semiconducting property. Moreover, as-prepared fluorescent Ag nanoclusters have been utilized as an indicator for selective and ultrasensitive detection of highly toxic HgII ions in water, even at subnanomolar concentrations.

# Photophysical Properties of Acene DCDHF Fluorophores:  Long-Wavelength Single-Molecule Emitters Designed for Cellular Imaging\_2007

Doping of fluorescent noble metal nanoclusters is being pursued to manipulate the structure of such materials along with improving physicochemical characteristics such as long-term stability and photoluminescence quantum yield. Here, we synthesize metal-doped and alloyed ultrasmall gold nanoclusters (AuNCs) directly in water using a facile one-step coreduction reaction with bidentate dithiolane PEGylated ligands that terminate in different functional groups including a methoxy, carboxy, amine, and azide. Two primary types of cluster materials were the focus of synthesis and characterization: first, a series of doped/alloyed Ag-doped AuNCs, where the ratio of Au:Ag was varied across a wide range including 99:1, 98:2, 90:10, 80:20, 50:50, 20:80, 10:90, and 2:98 along with pure AuNC and AgNC controls; second, doped Au:D NCs, where D included Pt, Cu, Zn, and Cd. Physical characterization of the modified AuNCs included TEM analysis of size, XPS/EDX analysis of dopant content, and a detailed analysis of photophysical properties including absorption and photoluminescence profiles, quantum yields over time, photoluminescence lifetimes, and examination of energy levels for selected materials. The addition of just a few Ag dopant atoms per AuNC yielded significant enhancement in quantum yield along with improving long-term photostability especially in comparison to materials with a very high Ag content. Preliminary cell imaging applications of the Ag-doped AuNCs were also investigated. Facilitated cellular uptake by mammalian cells via endocytosis following modification with cell penetrating peptides was confirmed by colabeling with specific cellular markers. Long-term intracellular photostability and lack of aggregation were confirmed with microinjection studies, and cytoviability assays showed the doped clusters to be minimally toxic.

# Facile Synthesis of Water-Soluble Fluorescent Silver Nanoclusters and HgII Sensing\_2010

Novel fluorogenic dyes based on the GFP chromophore are developed. The compounds contain a pyridinium ring instead of phenolate and feature large Stokes shifts and solvent-dependent variations in the fluorescence quantum yield. Electronic structure calculations explain the trends in solvatochromic behavior in terms of the increase of the dipole moment upon excited-state relaxation in polar solvents associated with the changes in bonding pattern in the excited state. A unique combination of such optical characteristics and lipophilic properties enables using one of the new dyes for imaging the membrane structure of endoplasmic reticulum. An extremely high photostability (due to a dynamic exchange between the free and absorbed states) and selectivity make this compound a promising label for this type of cellular organelles.

# Synthesis and Characterization of PEGylated Luminescent Gold Nanoclusters Doped with Silver and Other Metals\_2016

RNA-cleaving DNAzymes have been demonstrated as a promising platform for sensing metal ions. However, the poor biological imaging performance of RNA-cleaving DNAzyme-based fluorescent probes has limited their intracellular applications. Compared with traditional one-photon fluorescence imaging, two-photon (TP) fluorescent probes have shown advantages such as increased penetration depth, lower tissue autofluorescence, and reduced photodamage. Herein, for the first time, we developed an RNA-cleaving DNAzyme-based TP imaging probe (TP-8–17ES–AuNP) for Zn2+ detection in living cells by modifying a Zn2+-specific DNAzyme (8–17) with a TP fluorophore (TP-8–17ES) and using gold nanoparticles (AuNPs) for intracellular delivery. The modified TP-8–17ES exhibits good two-photon properties and excellent photostability. For the TP-8–17ES–AuNP, in the absence of Zn2+, the TP fluorophore is quenched by both AuNPs and the molecular quencher. Only in the presence of Zn2+ does the DNAzyme cleave the TP fluorophore-labeled substrate strand, resulting in fluorescence enhancement and TP imaging. Such probe shows remarkable selectivity of Zn2+ over other metal ions existing in the biological environment. Benefiting from the labeled TP fluorophore, the near-infrared (NIR) excited probe has the capability of TP imaging of Zn2+ in living cells and tissue with a deep tissue penetration up to 160 μm. This method can be generally applied to detect other metal ions in biological systems under TP imaging with higher tissue penetration ability and lower phototoxicity.

# Pyridinium Analogues of Green Fluorescent Protein Chromophore: Fluorogenic Dyes with Large Solvent-Dependent Stokes Shift\_2018

Organo-lead halide perovskite has emerged as a promising optical gain media. However, continuous efforts are needed to improve the amplified spontaneous emission (ASE) even lasing properties to evade the poor photostability and thermal instability of the perovskites. Herein, we report that simply through the coating of polymer layer, the CH3NH3PbBr3 polycrystalline films prepared by a modified sequential deposition process show remarkably enhanced photoluminescence and prolonged decay lifetime. As a result, under nanosecond pulse pumping, the ASE threshold of the perovskite films is significantly reduced from 303 to 140 μJ/cm2. Furthermore, the light exposure stability is improved greatly after the polymer coating. We confirmed that the polymer layer plays the roles of both surface passivation and symmetric waveguides. Our results may shed light upon the stable and sustained output of laser from perovskite materials.

# Two-Photon DNAzyme–Gold Nanoparticle Probe for Imaging Intracellular Metal Ions\_2018

It has been a long-lasting debate whether indigo undergoes excited-state proton transfer and how this contributes to its photostability. A prevailing point of view is that a sub-picosecond excited-state intramolecular single proton transfer occurs; however, it has been studied mostly under dilute solution conditions. In this work, excited-state structural dynamics of indigo oligomers formed at millimolar concentration in dimethyl sulfoxide is investigated using femtosecond visible pump spectroscopy, infrared and visible probe spectroscopies, and steady-state infrared and fluorescence spectroscopies. Experimental evidence indicates the presence of transient intermolecular electronic excited-state proton transfer, which is supported by quantum-chemistry computations. The formed enol species disappears with a time constant of 200–300 fs, followed by a relatively slow nonradiative relaxation to the electronic ground state. Our results reveal new photochemistry of indigo particularly in its oligomeric state.

# Simple Approach to Improving the Amplified Spontaneous Emission Properties of Perovskite Films\_2016

Microcapsules of the herbicide picloram (PLR) were formulated by a layer-by-layer (LbL) self-assembly method using the polyelectrolyte biopolymers of biocompatible chitosan (CS) and the UV-absorbent sodium lignosulfonate (SL) as shell materials. The herbicide PLR was recrystallized and characterized using XRD analysis. The obtained PLR-loaded microcapsules were characterized by using SEM, FTIR, CLSM, and ζ-potential measurements. The herbicide loading and encapsulation efficiency were also analyzed for the PLR-loaded microcapsules. The influence of LbL layer numbers on herbicide release and photodegradation rates was investigated in vitro. The results showed that the release rates and photodegradation rates of PLR in microcapsules decreased with increasing number of CS/SL self-assembly layers. The results demonstrated that polyelectrolyte biopolymer-based LbL multilayer microcapsules can be a promising approach for the controlled release of PLR as well as other pesticides with poor photostability or short half-release time.

# Ultrafast Excited-State Intermolecular Proton Transfer in Indigo Oligomer\_2019

Water-dispersible nanomaterials with superbright photoluminescence (PL) emissions and narrow PL bandwidths are urgently desired for various imaging applications. Herein, for the first time, we prepared ultrasmall organosilica nanodots (OSiNDs) with an average size of ∼2.0 nm and ∼100% green-emitting PL quantum efficiency via a one-step hydrothermal treatment of two commercial reagents (a silane molecule and rose bengal). In particular, the structural reorganization and halide loss of rose bengal during the hydrothermal treatment contribute to the ultrahigh quantum yield and low phototoxicity of OSiNDs. Owing to their low pH-induced precipitation/aggregation property, the as-prepared OSiNDs can be used as excellent lysosomal trackers with many advantages: (1) They have superior lysosomal targeting ability with a Pearson’s coefficient of 0.98; (2) The lysosomal monitoring time of OSiNDs is up to 48 h, which is much longer than those of commercial lysosomal trackers (<2 h); (3) They do not disturb the pH environment of lysosomes and can be used to visualize lysosomes in living, fixed, and permeabilized cells; (4) They exhibit intrinsic lysosomal tracking ability without the introduction of lysosome-targeting ligands (such as morpholine) and superior photostability; (5) The easy, cost-effective, and scalable synthetic method further ensures that these OSiNDs can be readily used as exceptional lysosomal trackers. We expect that the ultrasmall OSiNDs with superior fluorescence properties and easily modifiable surfaces could be applied as fluorescent nanoprobes, light-emitting diode phosphor, and anticounterfeiting material, which should be able to promote the preparation and application of silicon-containing nanomaterials.

# Encapsulation of the Herbicide Picloram by Using Polyelectrolyte Biopolymers as Layer-by-Layer Materials\_2013

Microbial colonization of biomedical devices is a recognized complication contributing to healthcare-associated infections. One of the possible approaches to prevent surfaces from the biofilm formation is antimicrobial photodynamic inactivation based on the cytotoxic effect of singlet oxygen, O2(1Δg), a short-lived, highly oxidative species, produced by energy transfer between excited photosensitizers and molecular oxygen. We synthesized porphyrin-based covalent organic frameworks (COFs) by Schiff-base chemistry. These novel COFs have a three-dimensional, diamond-like structure. The detailed analysis of their photophysical and photochemical properties shows that the COFs effectively produce O2(1Δg) under visible light irradiation, and especially three-dimensional structures have strong antibacterial effects toward Pseudomonas aeruginosa and Enterococcus faecalis biofilms. The COFs exhibit high photostability and broad spectral efficiency. Hence, the porphyrinic COFs are suitable candidates for the design of antibacterial coating for indoor applications.

# One-Step Synthesis of Ultrasmall and Ultrabright Organosilica Nanodots with 100% Photoluminescence Quantum Yield: Long-Term Lysosome Imaging in Living, Fixed, and Permeabilized Cells\_2018

We report the observation of individual steps taken by motor proteins in living cells by following movements of endocytic vesicles that contain quantum dots (QDs) with a fast camera. The brightness and photostability of quantum dots allow us to record motor displacement traces with 300 μs time resolution and 1.5 nm spatial precision. We observed individual 8 nm steps in active transport toward both the microtubule plus- and minus-ends, the directions of kinesin and dynein movements, respectively. In addition, we clearly resolved abrupt 16 nm steps in the plus-end direction and often consecutive 16 nm and occasional 24 nm steps in minus-end directed movements. This work demonstrates the ability of the QD assay to probe the operation of motor proteins at the molecular level in living cells under physiological conditions.

# Designing Porphyrinic Covalent Organic Frameworks for the Photodynamic Inactivation of Bacteria\_2018

Lead halide perovskites have emerged as low-cost, high-performance optical and optoelectronic materials, however, their material stability has been a limiting factor for broad applications. Here, we demonstrate stable core–shell colloidal perovskite nanocrystals using a novel, facile and low-cost copolymer templated synthesis approach. The block copolymer serves as a confined nanoreactor during perovskite crystallization and passivates the perovskite surface by forming a multidentate capping shell, thus significantly improving its photostability in polar solvents. Meanwhile, the polymer nanoshell provides an additional layer for further surface modifications, paving the way to functional nanodevices that can be self-assembled or lithographically defined.

# Observation of Individual Microtubule Motor Steps in Living Cells with Endocytosed Quantum Dots\_2005

In the recent past, visible-light-mediated photoredox catalysis has made a huge impact on the development of new synthetic methods under very mild and ecologically benign conditions. Although semiconductor nanocrystals or quantum dots (QDs) possess suitable optoelectronic and redox properties for photoredox catalytic applications, surprisingly, their use for the activation of challenging chemical bonds in the synthesis of organic molecules is little explored. We report here the application of ZnSe/CdS core/shell QDs for the synthetically important photoredox catalytic activation of carbon–halogen bonds in dehalogenation and C–H arylation reactions using (hetero)aryl halides as bench-stable inexpensive bulk starting materials, under very mild reaction conditions. The outstanding catalytic activity of ZnSe/CdS core/shell QDs is a direct consequence of the high specific surface area and homogeneity of QDs in solution and their high photostability toward oxidation.

# Synthesis and Stabilization of Colloidal Perovskite Nanocrystals by Multidentate Polymer Micelles\_2017

In this study, a polyurethane emulsifer with various functional groups was prepared from isophorone diisocyanate, avermectin, 2,2-dimethylol propionic acid, and bis(2-hydroxyethyl) disulfide. The chemical structure of the polymer was confirmed by Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, and element analysis. The polymer exhibited adequate emulsification ability for avermectin after neutralization with triethylamine. A satisfaying nanoemulsion was obtained, in which avermectin was encapsulated in nanoparticles with 50 wt % drug loading, low organic solvent content, and high stability under dilution and centrifuging treatment in addition to low surface tension, high affinity to crop leaf, and improved avermectin photostability. The resulting nanoparticles showed degradability in the presence of dl-dithiothreitol or inside the insect as a result of the disulfide bonds, promoting the release of avermectin. As a result, the avermectin nanoparticles showed higher insecticidal ability compared to both the avermectin nanoparticles without a disulfide group and the avermectin emulsifiable concentrate.

# Quantum Dots in Visible-Light Photoredox Catalysis: Reductive Dehalogenations and C–H Arylation Reactions Using Aryl Bromides\_2017

The application of fluorescent probes is limited due to the small Stokes shifts and aggregation-caused quenching (ACQ) effect when accumulated in cells. Herein, a novel colorimetric and turn-on fluorescent probe based on salicylaldehyde azine with both aggregation-induced emission (AIE) and excited-state intramolecular proton transfer (ESIPT) properties for Cys/Hcy is proposed to solve these issues. This probe showed a large Stokes shift (148 nm), low cytotoxicity as well as outstanding photostability upon recognition and the response mechanism was confirmed by fluorescence spectroscopy, High performance liquid chromatography (HPLC), thin layer chromotography (TLC), and transmission electron microscope (TEM). In addition to being used for cell imaging, a simple and user-friendly portable kit based on this probe was proposed as a new tool for the on-site inspection of more than ten microsamples simultaneously, which could effectively prevent the occurrence of false positives and visual errors.

# Fabrication of Novel Avermectin Nanoemulsion Using a Polyurethane Emulsifier with Cleavable Disulfide Bonds\_2017

A large anionic UV absorbent has been intercalated into a layered double hydroxide (LDHs) host by ion-exchange of an Zn−Al LDHs-nitrate precursor with a solution of 2-naphthylamine-1,5-disulfonic acid in water. After intercalation of the UV absorbent, the powder X-ray diffraction (XRD) pattern shows that the interlayer distance in the LDHs increases from 0.90 to 1.56 nm. The possible structure is that the interlayer NADA anions arrange in a monolayer and a slantwise orientation toward the hydroxide layers. Infrared spectra and TG-DTA curves reveal the presence of a complex system of supramolecular host−guest interactions between layers. The thermal stability of the intercalated UV absorbent was investigated by TG-DTA and it was found that this material is more stable than the pure UV absorbent at high temperature, showing that the thermostability is markedly enhanced after intercalation into the LDHs host. The UV absorbent-intercalated LDHs exhibit excellent UV photostability in polypropylene composites.

# A Novel AIE Plus ESIPT Fluorescent Probe with a Large Stokes Shift for Cysteine and Homocysteine: Application in Cell Imaging and Portable Kit\_2018

Perovskite quantum dots (PQDs) are among the most important luminescent semiconducting materials; however, they are unstable. Exposure to light, heat, and air can lead to irreversible degradation, which results in fluorescence quenching. Therefore, defects in PQDs significantly limit their practical application. Herein, we describe a simple method to enhance the photostability of CsPbBr3/nCdS QDs, which involves doping their shells with aluminum. The temperature-dependent photoluminescence (PL) of colloidal CsPbBr3/nCdS/Al2O3 QDs is investigated, and the thermal quenching of PL, blue shift of the optical band gap, and PL line width broadening are observed in each QD sample. Al2O3 layers on the CsPbBr3/nCdS QDs can effectively prevent photodegradation. Nonlinear, temperature-dependent exciton–phonon coupling and lattice dilation leads to radiative and nonradiative relaxation processes at temperatures ranging from 10 to 300 K; moreover, changes in the band gap and PL spectral line broadening are observed.

# Synthesis and UV Absorption Properties of 2-Naphthylamine-1,5-disulfonic Acid Intercalated Zn−Al Layered Double Hydroxides\_2008

The effective separation and transport of photoinduced electron–hole pairs in photoanodes is of great significance to photoelectrochemical and catalytic performance. Here, a facile and effective two-step strategy is developed to fabricate double-shelled ZnO/CdS/CdSe porous nanotube photoanodes from ZnO nanorod arrays (NRAs). Surprisingly, after the process of the deposition of CdS and CdSe, the ZnO nanorod arrays are partially dissolved, resulting in the formation of ZnO/CdS/CdSe porous nanotube arrays (NTAs). By virtue of their unique porous nanotube structure and cosensitization effect, the ZnO/CdS/CdSe porous NTAs show superior photoelectrochemical water-splitting performance and organic-pollutant-degradation ability under visible light irradiation, as well as excellent long-term photostability.

# Stable Luminescence of CsPbBr3/nCdS Core/Shell Perovskite Quantum Dots with Al Self-Passivation Layer Modification\_2019

The superoxide anion (O2•–) and hydroxyl radical (•OH) are important reactive oxygen species (ROS) used as biomarkers in physiological and pathological processes. ROS generation is closely related to the development of a variety of inflammatory diseases. However, the changes of ROS are difficult to ascertain with in situ tracing of the inflammation process by real-time monitoring, owing to the short half-lives of ROS and high tissue autofluorescence in vivo. Here we developed a new near-infrared (NIR) ratiometric fluorescence imaging approach by using a Förster resonance energy transfer (FRET)-based ratiometric fluorescent nanoprobe for real-time monitoring of O2•– and •OH generation and also by using in situ tracing of the inflammation process in vivo. The proposed nanoprobe was composed of PEG functionalized GQDs as the energy donor connecting to hydroIR783, serving as both the O2•–/•OH recognizing ligand and the energy acceptor. The nanoprobe not only exhibited a fast response to O2•– and •OH but also presented good biocomapatibility as well as a high photostability and signal-to-noise ratio. We have demonstrated that the proposed NIR ratiometric fluorescent nanoprobe can monitor the changes of O2•– and •OH in living RAW 264.7 cells via a drug mediating inflammation model and further realized visual monitoring of the change of O2•– and •OH in mice for in situ tracing of the inflammation process. Our design may provide a new paradigm for long-term and real-time imaging applications for in vivo tracing of the pathological process related to the inflammatory diseases.

# Double-Shelled CdS- and CdSe-Cosensitized ZnO Porous Nanotube Arrays for Superior Photoelectrocatalytic Applications\_2015

A series of star-shaped octupolar triazatruxenes (TATs, 1−6) with intramolecular “push−pull” structure were synthesized and their photophysical properties have been systematically investigated. These chromophores showed obvious solvatochromic effect, i.e., significant bathochromic shift of the emission spectra and larger Stokes shifts were observed in more polar solvents mainly due to photoinduced intramolecular charge transfer (ICT). The two-photon absorption (2PA) cross-section values were determined by two-photon excited fluorescence (2PEF) measurements in toluene and THF. These chromophores exhibited large two-photon absorption cross-sections ranging from 280 to 1620 GM in the near-infrared (NIR) region. Compound 6 showed the largest 2PA action cross-section (σ2Φ) of 564 GM and could be a potential two-photon fluorescent (2PF) probe. In addition, compounds 1−6 all displayed good thermal stability and photostability.

# Design of a New Near-Infrared Ratiometric Fluorescent Nanoprobe for Real-Time Imaging of Superoxide Anions and Hydroxyl Radicals in Live Cells and in Situ Tracing of the Inflammation Process in Vivo\_2018

Dynamic developments in ultrasensitive and superresolution fluorescence microscopy call for improved fluorescence markers with increased photostability and new functionalities. We used single-molecule spectroscopy to study water-soluble perylene dicarboximide fluorophores (PDI), which were immobilized in aqueous buffer by attaching the fluorophore to DNA. Under these conditions bright fluorescence, comparable to that of single-molecule compatible organic fluorophores, is observed with homogeneous spectral and fluorescence decay time distributions. We additionally show how the fluorescence of the PDI can be controlled through photoinduced electron-transfer reactions by using different concentrations of reductants and oxidants, yielding either blinking or stable emission. We explain these properties by the redox potentials of PDI and the recently introduced ROXS (reducing and oxidizing system) concept. Finally, we evaluate how this fluorescence control of PDIs can be used for superresolution “Blink-Microscopy” in aqueous or organic media and more generally for single-molecule spectroscopy.

# Synthesis and Characterizations of Star-Shaped Octupolar Triazatruxenes-Based Two-Photon Absorption Chromophores\_2011

Multicolor polymer nanoparticles (or dots) were prepared via the reaction between hyperbranched polyethyleneimine (PEI) and aldehydes, and when the concentration of aldehydes was lower, the final mixture displayed gelation behavior. This phenomenon can be applied to visual detection of aldehydes. Moreover, the colors of the polymer dots and gel are varied by using different kinds of aldehydes, which can be utilized for visual discrimination of aldehydes. For simplicity, we focus our attention on the interaction between PEI and formaldehyde. The nanoparticles show an average diameter of 42 nm, emit bright cyan fluorescence with high quantum yield, and exhibit high water dispersibility and excellent photostability. Due to the advantages, our polymer nanoparticles (PNPs) are utilized as a fluorescent probe for imaging in living SK-N-SH cells. Furthermore, valuable explorations have been carried out on the fundamental properties of PNPs, such as concentration-dependent fluorescence, pH-dependent fluorescence, and solvent effect.

# Single-Molecule Redox Blinking of Perylene Diimide Derivatives in Water\_2010

A great deal of thermally instable cis form photoisomerization products will be formed from the thermally stable trans form of the plant sunscreens sinapate esters upon ultraviolet radiation. To reveal the photoisomerization mechanism of the cis-isomer, we explore the photodynamics of a model plant sunscreen methyl sinapate (MS) in the cis form in organic solution. The high photoisomerization quantum yield of the cis-isomer results in the relatively higher photostability of trans-MS. By utilizing femtosecond transient absorption spectroscopy and quantum chemical calculation, we propose that an adiabatic relaxation competes with nonadiabatic relaxation for the excited-state cis form of methyl sinapate. These results suggest that the photoprotection mechanism of the cis form of sinapate esters is significantly different from that of the trans form of sinapate esters and plays an important role in the overall photoprotection effect.

# Diverse States and Properties of Polymer Nanoparticles and Gel Formed by Polyethyleneimine and Aldehydes and Analytical Applications\_2015

Organic metal halide hybrids with zero-dimensional (0D) structure at the molecular level, or single-crystalline bulk assemblies of metal halides, are an emerging class of light-emitting materials with high photoluminescence quantum efficiencies (PLQEs) and color tunability. Here we report the synthesis and characterization of a new single-crystalline bulk assembly of metal halide clusters, (bmpy)9[ZnCl4]2[Pb3Cl11] (bmpy: 1-butyl-1-methylpyrrolidinium), which exhibits green emission peaked at 512 nm with a remarkable near-unity PLQE at room temperature. Detailed structural and photophysical studies suggest that there are two emitting states in [Pb3Cl11]5– clusters, whose populations are strongly dependent on the surrounding molecular environment that controls the excited-state structural distortion of [Pb3Cl11]5– clusters. High chemical- and photostability have also been demonstrated in this new material.

# New Insight into the Photoprotection Mechanism of Plant Sunscreens: Adiabatic Relaxation Competing with Nonadiabatic Relaxation in the cis → trans Photoisomerization of Methyl Sinapate\_2019

Aqueous suspensions of highly luminescent Eu3+ chelate nanoparticles are prepared by a novel reprecipitation−encapsulation method. An alkyl alkoxysilane encapsulation agent is included during the nanoparticle formation process, forming a nanoparticle encapsulation layer that inhibits aggregation as evidenced by UV−vis spectroscopy and atomic force microscopy. In addition, the encapsulated nanoparticles exhibit a small size (10 nm), intense luminescence, and excellent photostability. We estimate that the molar extinction coefficients of the ∼10 nm particles are approximately 5.0 × 107 M-1 cm-1 with a luminescence quantum yield of 6%, indicating a luminescence brightness many times larger than that of conventional fluorescent dyes and comparable to that of colloidal semiconductor quantum dots. The small size, high brightness, highly red-shifted luminescence, and long luminescence lifetimes of the nanoparticles are of interest for luminescence labeling and sensing applications.

# Green Emitting Single-Crystalline Bulk Assembly of Metal Halide Clusters with Near-Unity Photoluminescence Quantum Efficiency\_2019

We present the first example of water soluble complexes of carotenoids. The stability and reactivity of carotenoids in the complexes with natural polysaccharide arabinogalactan were investigated by different physicochemical techniques: optical absorption, HPLC, and pulsed EPR spectroscopy. Compared to pure carotenoids, polysaccharide complexes of carotenoids showed enhanced photostability by a factor of 10 in water solutions. A significant decrease by a factor of 20 in the reactivity toward metal ions (Fe3+) and reactive oxygen species in solution was detected. On the other hand, the yield and stability of carotenoid radical cations photoproduced on titanium dioxide (TiO2) were greatly increased. EPR measurements demonstrated efficient charge separation on complex-modified TiO2 nanoparticles (7 nm). Canthaxanthin radical cations are stable for ∼10 days at room temperature in this system. The results are important for a variety of carotenoid applications, in the design of artificial light-harvesting, photoredox, and catalytic devices.

# Highly Luminescent Eu3+ Chelate Nanoparticles Prepared by a Reprecipitation−Encapsulation Method\_2007

Molybdenum disulfide (MoS2) quantum dots (QDs) derived from this two-dimensional (2D) transition metal dichalcogenide are emerging zero-dimensional materials that possess very good optical properties. Bioimaging using light in the biological II window (950–1350 nm) is a next-generation approach that will allow clinicians to achieve deeper tissue imaging with better image contrast and reduced phototoxicity and photobleaching. This article reports the development of a water-soluble, zero-dimensional antibody-conjugated transition metal dichalcogenide MoS2 QD-based two-photon luminescence (TPL) probe for the targeted bioimaging of cancer cells in the biological II window. The data indicates that MoS2 QDs exhibit an extremely high two-photon absorption cross-section (σ = 58960 GM) and two-photon brightness (4.7 × 103 GM) because of the quantum confinement and edge effects. Experimental data show that anti-PSMA antibody-attached MoS2 QDs can be used for selective two-photon imaging of live prostate cancer cells using 1064 nm light because of the high two-photon brightness, very good photostability, and very good biocompatibility of these MoS2 QDs. The data demonstrate that the bioconjugated MoS2 QDs can distinguish targeted and nontargeted cells. This study illuminates the high two-photon brightness mechanism of MoS2 QDs and provides a zero-dimensional transition metal dichalcogenide-based selective TPL agent for high-efficiency live cell imaging.

# Water Soluble Complexes of Carotenoids with Arabinogalactan\_2008

We studied surface plasmon-coupled emission (SPCE) of semiconductor quantum dots (QDs). These QDs are water-soluble ZnS-capped CdSe nanoparticles stabilized using lysine cross-linked mercaptoundecanoic acid. The QDs were spin-coated from 0.75% PVA solution on a glass slide covered with 50 nm of silver and a 5-nm protective SiO2 layer. Excited QDs induced surface plasmons in a thin silver layer. Surface plasmons emitted a hollow cone of radiation into an attached hemispherical glass prism at a narrow angle of 48.5°. This directional radiation (SPCE) preserves the spectral properties of QD emission and is highly p-polarized irrespective of the excitation polarization. The SPCE spectrum depends on the observation angle because of the intrinsic dispersive properties of SPCE phenomenon. The remarkable photostability can make QDs superior to organic fluorophores when long exposure to the intense excitation is needed. The nanosize QDs also introduce a roughness near the metal layer, which results in a many-fold increase of the coupling of the incident light to the surface plasmons. This scattered incident illumination transformed into directional, polarized radiation can be used simultaneously with SPCE to develop devices based on both quantum dot emission and light scattered from surface plasmons on a rough surface.

# Two-Photon Fluorescent Molybdenum Disulfide Dots for Targeted Prostate Cancer Imaging in the Biological II Window\_2017

We demonstrate the synthesis of near-IR-emitting zinc blende CdTe/CdS tetrahedral-shaped nanocrystals with a magic-sized (∼0.8 nm radius) CdTe core and a thick CdS shell (up to 5 nm). These high-quality water-soluble nanocrystals were obtained by a simple but reliable aqueous method at low temperature. During the growth of the shell over the magic core, the core/shell nanocrystals change from type I to type II, as revealed by their enormous photoluminescence (PL) emission peak shift (from 480 to 820 nm) and significant increase in PL lifetime (from ∼1 to ∼245 ns). These thick-shell nanocrystals have a high PL quantum yield, high photostability, compact size (hydrodynamic diameter less than 11.0 nm), and reduced blinking behavior. The magic-core/thick-shell nanocrystals may represent an important step toward the synthesis and application of next-generation colloidal nanocrystals from solar cell conversion to intracellular imaging.

# Surface-Plasmon-Coupled Emission of Quantum Dots\_2004

Dark azido push−pull chromophores have the ability to be photoactivated to produce bright fluorescent labels suitable for single-molecule imaging. Upon illumination, the aryl azide functionality in the fluorogens participates in a photochemical conversion to an aryl amine, thus restoring charge-transfer absorption and fluorescence. Previously, we reported that one compound, DCDHF-V-P-azide, was photoactivatable. Here, we demonstrate that the azide-to-amine photoactivation process is generally applicable to a variety of push−pull chromophores, and we characterize the photophysical parameters including photoconversion quantum yield, photostability, and turn-on ratio. Azido push−pull fluorogens provide a new class of photoactivatable single-molecule probes for fluorescent labeling and super-resolution microscopy. Lastly, we demonstrate that photoactivated push−pull dyes can insert into bonds of nearby biomolecules, simultaneously forming a covalent bond and becoming fluorescent (fluorogenic photoaffinity labeling).

# Aqueous Synthesis of Zinc Blende CdTe/CdS Magic-Core/Thick-Shell Tetrahedral-Shaped Nanocrystals with Emission Tunable to Near-Infrared\_2010

Accurately characterizing the product of photodecomposition of ferrocene derivatives remains a longstanding challenge due to its structural complexity and strong dependence on the solvent and the substituent. Herein, photodecomposition of ferrocenedicarboxylic acid (FcDC) in methanol is found for the first time to form an electroactive infinite coordinate polymer (ICP) with uniform size, good water stability and photostability, and excellent electrochemical activity. The possible mechanism for the ICP formation is proposed based on the fission of the Fe-ring bond and deprotonation of FcDC under light irradiation. The dissociated Fe2+ is first oxidized to Fe3+ that consequently coordinates with the deprotonated ferrocene dicarboxylate to produce ICP nanoparticles. This work not only provides a new insight into the product formation of the photodecomposition of ferrocene derivatives but also offers a mild and simple route to the synthesis of electroactive ICPs.

# Azido Push−Pull Fluorogens Photoactivate to Produce Bright Fluorescent Labels\_2009

Poly(phenylenevinylene)s (PPVs) containing rigid oxadiazole units as main chain substituents were synthesized. The electron-deficient oxadiazole moieties are directly attached to the phenyl rings of PPVs to increase the electron-injection properties of the polymers. In addition, the near-orthogonal arrangement of the PPV backbone and the oxadiazole units helps to limit the π-stacking of the emissive units, thus increasing the radiative decay quantum yield and photostability of the polymer. These polymers have shown good electron injection/transport ability and luminescence properties. Single-layer LED devices with the configuration ITO/polymer/Al show external quantum efficiencies up to 0.045%.

# Photodecomposition of Ferrocenedicarboxylic Acid in Methanol to Form an Electroactive Infinite Coordination Polymer and Its Application in Bioelectrochemistry\_2013

Suzuki–Miyaura polycondensation of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-bromo-9,9-dioctylfluorene in aqueous miniemulsion with only two equivalents of NaOH as a base yields colloidally stable nanoparticles of polyfluorene with Mn ca. 2 × 104 g mol–1 and particle sizes of 40–85 nm, depending on the surfactant concentration. Polymerization in the presence of CdSe/CdS core/shell quantum dots affords hybrid nanoparticles of nonaggregated quantum dots, in particular nanoparticles composed of a single quantum dot embedded in a polyfluorene shell. Microphotoluminescence spectroscopy on single hybrid particles reveals an enhanced photostability of the quantum dots and indicates an efficient Förster energy transfer from the polyfluorene shell to the quantum dot.

# New Oxadiazole-Containing Conjugated Polymer for Single-Layer Light-Emitting Diodes\_1999

A series of novel heterocyclic polymers with fluorescent brightening properties are synthesized via Click polymerization. Fast synthesis of poly-1,2,3-triazoles (Mn ≥ 9.31 kDa) is described herein, with a high yield of up to 95%. The Click polymerization approach has a number of advantages, including facile operation and outstanding isolation yield. The resultant polymers have a high thermal stability, excellent UV resistance, as well as acid and light fastness. On embedding with optical brightening agents, the polymers display strong fluorescent brightening properties in the tetrahydrofuran solution. Moreover, these products have a strong solution emission intensity and extraordinary photostability under UV light.

# Polyfluorene Nanoparticles and Quantum Dot Hybrids via Miniemulsion Polymerization\_2012

An ultraviolet (UV) filter is the core component of sunscreen and protects skin from various photo damages. Current UV filters are hampered by skin penetration, poor photostability, photocatalytic generation of harmful reactive oxygen species (ROS), and potential environmental risks. In this work, manganese dioxide nanoclusters were developed as an eco-friendly UV filter by a facile two-step synthesis, using colloid silica as support under ambient conditions. These nanoclusters show a better UV-shielding profile than commercial titanium dioxide nanoparticles and capability to scavenge various ROS. They can be easily incorporated by a sunscreen formula and demonstrate an excellent skin photoprotection performance both in vitro and in vivo.

# Preparation and Characterization of Poly-1,2,3-triazole with Chiral 2(5H)-Furanone Moiety as Potential Optical Brightening Agents\_2017

Nonlinear optical behavior of a novel nanocomposite material based on chloroaluminum phthalocyanine (ClAlPc) embedded in silica and incorporated in the structural nanopores of a Nafion membrane is investigated using the Z-scan technique. The experiments are performed at 532 nm using 8 ns pulses at a pulse repetition rate of 10 Hz from a frequency-doubled Nd:YAG laser. The nonlinearity in the hybrid membranes is characterized by obtaining the nonlinear refractive index and nonlinear absorption coefficient. Fluorescence lifetimes are measured using a time-correlated single photon counting technique. The effects of dynamic and static quenching on photostability are studied. Incorporating phthalocynanine molecules in the stable hybrid membrane renders them stable against photobleaching and provides a convenient solid matrix.

# Manganese Oxide Nanoclusters for Skin Photoprotection\_2019

A fundamental, highly fluorescent, and easily accessible scaffold named BOPPY is reported. The use of hydrazine as a bridging linkage between pyrrole and N-heteroarenes enables the binding of two BF2 units to provide sufficient rigidity of the unsymmetric core skeleton. These resultant unsymmetrical BOPPYs are thus highly fluorescent in their solutions and solid powder states and exhibit high molar absorption coefficients (42200–47000 M–1 cm–1), large Stokes shifts, excellent photostability, and insensitivity to pH. More importantly, these BOPPYs showed efficient two-photon absorption in the wide spectral range of 700–900 nm, making them well suited for two-photon fluorescence microscopy imaging in living cells.

# Nonlinear Refraction and Absorption Phenomena in a Novel Nanocomposite Based on a Dye Stabilized in a Solid Hybrid Matrix\_2008

The innocent silicon quantum dots (SQDs) having dual emissive property (blue in VIS and red in NIR), high photostability, and freedom from auto fluorescence are designed and synthesized for the first time using ethylene glycol. A new attempt has been made for direct labeling of Alpha 2-HS-Glycoprotein (Fetuin A) through functionalization of the synthesized dots by EDC coupling. The SQDs were characterized by FTIR, TEM, AFM, XRD, EDX, DLS, and TGA. The chemistry involved in the synthesis and functionalization of dots is elucidated in detail. The synthesized SQDs are suitable for live cell imaging as well as direct labeling of the Fetuin A in the NIR region. The direct labeling technique developed for Fetuin A imaging is robust, more specific, and simple, and reduces the number of incubation and washing steps and produces better quality data compared to the conventional method using Rhodamine B.

# A Family of Highly Fluorescent and Unsymmetric Bis(BF2) Chromophore Containing Both Pyrrole and N-Heteroarene Derivatives: BOPPY\_2018

Alloyed CdSxSe1–x semiconductor nanocrystals (NCs) were obtained from a one-pot synthesis at reduced temperature with moderate quantum yield. Comprehensive structural characterizations of the CdSSe NCs reveal that the NCs have gradient alloyed structure, with Cd evenly distributed over the entire NC, Se rich in the center, and S rich in the outer region. This is due to the difference in the nucleation kinetics of S and Se precursors. Optical studies at the single NC level show that the NCs have reduced photoluminescence blinking, increased “on” time fraction, and good photostability, in comparison with CdSe NCs. The incorporation of sulfur composition in the alloy NCs improves surface passivation and in turn protects the NCs from (photo)oxidation. The gradual change in the NC composition from center to outer regions creates a smooth “interface”, compared to core/shell NCs. These factors lead to reduced nonradiative rates in the NCs, improving their emitting properties.

# Designed Synthesis of Dual Emitting Silicon Quantum Dot for Cell Imaging: Direct Labeling of Alpha 2-HS-Glycoprotein\_2019

Maya Blue is a puzzling pigment found in objects produced by the ancient Maya civilization. It is a combination of indigo and palygorskite, and it is well-known for the high chemical and photochemical stability of the dye promoted by the clay confined environment. This pigment has survived over 1500 years, and it was first thought to be purely inorganic. The reasons for such stability have been investigated over the past years, and it may involve hydrogen bonds, complexation, and oxidation to dehydroindigo. However, these theories are not completely understood, and more evidence about indigo/palygorskite interactions must be obtained. In this study indigo and a Maya Blue simulant pigment were, for the first time, studied by transient absorption (TA) and time-resolved infrared (TRIR) spectroscopy. From such analysis it was possible to investigate the electronic excited states of indigo and the photochemistry behavior of the dye when interacting with the palygorskite. Concerning the TRIR measurements, the shifts of the C═O and N–H vibrations indicate that hydrogen bonds are formed involving the dye and the coordinated water molecules present in the clay. Furthermore, a red shift is observed in the absorption of electronic ground state (50 nm) and also in the electronic excited state (27 nm) of Maya Blue simulant, suggesting that the excited states are stabilized by the clay. Indigo in DMSO solution presents a lifetime of ca. 120 ps while in the clay it becomes much shorter, ca. 3 ps. The shorter lifetime and also the red shift observed in the TA results suggest a stabilization of the first electronic excited state, which promotes a more efficient energy relaxation through conical intersection and, as a consequence, a faster excited state decay. Such factors can be important for the Maya Blue photostability, as they are also believed to be responsible for the high photostability of DNA and melanin.

# Effect of Gradient Alloying on Photoluminescence Blinking of Single CdSxSe1–x Nanocrystals\_2016

Design and engineering of highly efficient light-harvesting nanomaterial systems to emulate natural photosynthesis for maximizing energy conversion have stimulated extensive efforts. Here we present a new class of photoactive semiconductor nanocrystals that exhibit high-efficiency energy transfer for enhanced photocatalytic hydrogen production under visible light. These nanocrystals are formed through noncovalent self-assembly of In(III) meso-tetraphenylporphine chloride (InTPP) during microemulsion assisted nucleation and growth process. Through kinetic control, a series of uniform nanorods with controlled aspect ratio and high crystallinity have been fabricated. Self-assembly of InTPP porphyrins results in extensive optical coupling and broader coverage of the visible spectrum for efficient light harvesting. As a result, these nanocrystals display excellent photocatalytic hydrogen production and photostability under the visible light in comparison with the commercial InTPP porphyrin powders.

# Microemulsion-Assisted Self-Assembly and Synthesis of Size-Controlled Porphyrin Nanocrystals with Enhanced Photocatalytic Hydrogen Evolution\_2019

Formaldehyde (FA), in the 0.2–0.4 mM range, is produced and maintained endogenously via enzymatic pathways. At these levels, FA can promote cell proliferation as well as mediate memory formation. Once elevated, FA stress is known to induce cognitive impairments, memory loss, and neurodegeneration owing to its potent DNA and protein cross-linking mechanisms. Optical imaging is a powerful noninvasive approach used to study FA in living systems; however, biocompatible chemical probes for FA are currently lacking. Herein, we report the design, synthesis, and biological evaluation of Formaldehyde Probe 1 (FP1), a new fluorescent indicator based on the 2-aza-Cope sigmatropic rearrangement. The remarkable sensitivity, selectivity, and photostability of FP1 has enabled us to visualize FA in live HEK293TN and Neuroscreen-1 cells. We envision that FP1 will find widespread applications in the study of FA associated with normal and pathological processes.

# Time-Resolved Spectroscopy of Indigo and of a Maya Blue Simulant\_2016

RNA-binding small probes with deep-red emission are promising for RNA analysis in biological media without suffering from background fluorescence. Here benzo[c,d]indole–quinoline (BIQ), an asymmetric monomethine cyanine analogue, was newly developed as a novel RNA-selective probe with light-up signaling ability in the deep-red spectral range. BIQ features a significant light-up response (105-fold) with an emission maximum at 657 nm as well as improved photostability over the commercially available RNA-selective probe, SYTO RNA select. BIQ was successfully applied to the fluorescence imaging of nucleolar RNAs in living cells with negligible cytotoxicity. Furthermore, we found the useful ability of BIQ as a base surrogate integrated in peptide nucleic acid (PNA) oligonucleotides for RNA sequence analysis. BIQ base surrogate functioned as a deep-red light-up base surrogate in forced intercalation (FIT) and triplex-forming FIT (tFIT) systems for the sequence-selective detection of single-stranded and double-stranded RNAs, respectively.

# A Reaction-Based Fluorescent Probe for Imaging of Formaldehyde in Living Cells\_2015

A hyperbranched conjugated polyelectrolyte (HCPE) with a core–shell structure is designed and synthesized via alkyne polycyclotrimerization and click chemistry. The HCPE has an emission maximum at 565 nm with a quantum yield of 12% and a large Stokes shift of 143 nm in water. By virtue of its poly(ethylene glycol) shell, this polymer naturally forms spherical nanoparticles that minimize nonspecific interaction with biomolecules in aqueous solution, consequently allowing for efficient bioconjugation with anti-HER2 affibody via carbodiimide-activated coupling reaction. The resulting affibody-attached HCPE can be utilized as a reliable fluorescent probe for targeted cellular imaging of HER2-overexpressed cancer cells such as SKBR-3. Considering its low cytotoxicity and good photostability, the HCPE nanoprobe holds great promise in practical imaging tasks. This study also provides a molecular engineering strategy to overcome the intrinsic limitations of traditional fluorescent polymers (e.g., chromophore-tethered polymers and linear conjugated polyelectrolytes) for bioconjugation and applications.

# Deep-Red Light-up Signaling of Benzo[c,d]indole–Quinoline Monomethine Cyanine for Imaging of Nucleolar RNA in Living Cells and for Sequence-Selective RNA Analysis\_2019

With a fused terthiophene, dithieno[3,4-b:2′,3′-d]thiophene (DTT) is used as a thienoquinoidal building block for conjugated polymers. However, due to its highly extended heteroarene structure, chemical synthesis of the functional DTT unit is a challenge. All known DTT-based polymer films were prepared by an electrochemical polymerization approach. In this study, we first synthesized the functional DTT monomer and DTT-based conjugated polymer, PDBT-DTT, via a typical Stille coupling reaction. With another fused thiophene ring, DTT shows increased aromatic (weaker quinoid) character compared to the thieno-[3,4-b]thiophene (TT) unit. Moreover, PDBT-DTT showed much higher photovoltaic performance as well as better thermal and photostability than its TT-based analogue (PDBT-TT). The results demonstrate that DTT is a potential quinoidal building block for constructing high-performance conjugated polymers.

# Affibody-Attached Hyperbranched Conjugated Polyelectrolyte for Targeted Fluorescence Imaging of HER2-Positive Cancer Cell\_2011

A scalable method for controlled synthesis of luminescent compound semiconductor nanocrystals (quantum dots) using microemulsion−gas contacting at room temperature is reported. The technique exploits the dispersed phase of a microemulsion to form numerous identical nanoreactors. ZnSe quantum dots were synthesized by reacting hydrogen selenide gas with diethylzinc dissolved in the heptane nanodroplets of a microemulsion formed by self-assembly of a poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) amphiphilic block copolymer in formamide. A single nanocrystal is grown in each nanodroplet, thus allowing good control of particle size by manipulation of the initial diethylzinc concentration in the heptane. The ZnSe nanocrystals exhibit size-dependent luminescence and excellent photostability.

# Novel π-Conjugated Polymer Based on an Extended Thienoquinoid\_2018

We show that meso-to-meso ethyne-bridged (porphinato)zinc(II) oligomers (PZnn structures) define exceptional low band gap organic materials that possess both large magnitude NIR S1 → S0 fluorescence quantum yields and substantial S1 → Sn absorptive cross-sections, tunable over a wide 850−1400 nm spectral window. These PZnn species possess fluorescence quantum yields (φf values) comparable to the highest reported for NIR laser dyes in the 750−900 nm regime; importantly, these emitters do not suffer from commonly cited tricarbocyanine dye drawbacks of poor photostability and substantial φf sensitivity to solvent polarity. Furthermore, τo (kr-1) values determined using the Strickler−Berg method highlight the close correlation of fluorescence quantum yields with S0 → S1 integrated oscillator strength and demonstrate a rare if not unique example of broad NIR spectral domain fluorescence energy modulation, where φf magnitudes follow a simple Strickler−Berg relationship.

# Synthesis and Size Control of Luminescent ZnSe Nanocrystals by a Microemulsion−Gas Contacting Technique\_2004

Can polarity-sensitive fluorescent dyes monitor the response of live cells to fundamental stress conditions, such as deprivation from nutrition and oxidative stress? To address this question, we developed a push–pull dioxaborine probe (DXB-NIR) for biomembranes and lipid droplets featuring strong solvatochromism in the far-red to near-infrared region, high fluorescence brightness, photostability, and two-photon absorption cross section, reaching 13800 GM at 930 nm. In model membranes, DXB-NIR exhibits unprecedented 80 nm shift between liquid ordered and disordered membrane phases, allowing robust imaging of separated membrane microdomains. Two-color imaging of live cells with DXB-NIR enables polarity mapping in plasma membranes, endoplasmic reticulum, and lipid droplets, which reveals that starvation and oxidative stress produce an increase in the local polarity, and this change is different for each of the studied cell compartments. Thus, by pushing the limits of existing solvatochromic dyes, we introduce a concept of polarity mapping for monitoring the response of cells to stress.

# Exceptional Near-Infrared Fluorescence Quantum Yields and Excited-State Absorptivity of Highly Conjugated Porphyrin Arrays\_2006

Due to their greater photostability compared to established organic fluorescence markers, semiconductor quantum dots provide an attractive alternative for the biolabeling of living cells. On the basis of a comparative investigation using differently sized thiol-stabilized CdTe nanocrystals in a variety of commonly used biological buffers, a method is developed to quantify the stability of such a multicomponent system. Above a certain critical size, the intensity of the photoluminescence of the nanocrystals is found to diminish with pseudo-zero-order kinetics, whereas for specific combinations of particle size, ligand, and buffer there appears to be no decay below this critical particle size, pointing out the necessity for thorough investigations of this kind in the view of prospect applications of semiconductor nanocrystals in the area of biolabeling.

# Solvatochromic Near-Infrared Probe for Polarity Mapping of Biomembranes and Lipid Droplets in Cells under Stress\_2019

We have comparatively investigated the single-molecule photophysical properties of two chlorophyll trefoils that feature distinctive electronic couplings induced by differences in linkage: one is an ethynyl-linked chlorophyll trefoil (1) in which relatively short and rigid linkage between the chromophores promotes effective electronic coupling, and the other is a phenyl−ethynyl-linked chlorophyll trefoil (2) in which the phenyl addition induces an orthogonal geometry impeding π-conjugation and provides a longer interchlorophyll distance reducing through-space interaction. By recording single-molecule fluorescence intensity trajectories and their corresponding lifetimes, we observed one-step photobleaching behaviors, less frequent on−off behaviors, a narrower fluorescence lifetime distribution, and higher photostability in 1 as compared with 2. These results indicate that the performance of molecular photosynthetic systems in the solid state is strongly associated with electronic couplings and, thus, give insight into the construction of well-functioning artificial photosynthetic systems.

# Comparative Examination of the Stability of Semiconductor Quantum Dots in Various Biochemical Buffers\_2006

Red-emitting carbon dots (CDs) have attracted tremendous attention due to their wide applications in areas including imaging, sensing, drug delivery, and cancer therapy. However, it is still highly challenging for red-emitting CDs to simultaneously achieve high quantum yields (QYs), nucleus targeting, and super-resolution fluorescence imaging (especially the stimulated emission depletion (STED) imaging). Here, it is found that the addition of varied metal ions during the hydrothermal treatment of p-phenylenediamine (pPDA) leads to the formation of fluorescent CDs with emission wavelengths up to 700 nm. Strikingly, although metal ions play a crucial role in the synthesis of CDs with varied QYs, they are absent in the formed CDs, that is, the obtained CDs are metal-free, and the metal ions play a role similar to a “catalyst” during the CD formation. Besides, using pPDA and nickel ions (Ni2+) as raw materials, we prepare Ni–pPCDs which have the highest QY and exhibit various excellent fluorescence properties including excitation-independent emission (at ∼605 nm), good photostability, polarity sensitivity, and ribonucleic acid responsiveness. In vitro and in vivo experiments demonstrate that Ni–pPCDs are highly biocompatible and can realize real-time, wash-free, and high-resolution imaging of cell nuclei and high-contrast imaging of tumor-bearing mice and zebrafish. In summary, the present work may hold great promise in the synthesis and applications of red emissive CDs.

# Fluorescence Dynamics of Chlorophyll Trefoils in the Solid State Studied by Single-Molecule Fluorescence Spectroscopy\_2009

The nature and dynamics of DNA excited states is of pivotal importance in determining both DNA ultraviolet photostability and its vulnerability toward photodamage. The complexity regarding the involvement of “bright” and “dark” excited states, their molecular origin, and the roles played by these states in the course of electronic energy relaxation constitute an active and contentious area in current research of DNA excited states. As a case study, we report here a combined broadband femtosecond time-resolved fluorescence (TRF) and transient absorption (TA) study on a self-complementary d(AT)10 oligomer and a reference system of an equal molar mixture of the constituent bases represented by adenosine and thymidine (A+T). Comparison of the spectral character and temporal evolution of the TRF and TA data for 267 nm excited d(AT)10 and A+T provides evidence for a base-localized excitation feature for an early (<∼50 fs) “bright” SLE state and its ensuing evolution within ∼3 ps into a ∼72 ps “dark” SE exciplex in d(AT)10. Combined analysis of the d(AT)10 TRF and TA results suggests the presence of a weakly fluorescent transient SG state that acts as a gateway to mediate the excitation transfer and energy elimination. A distinct base conformation-dependent model involving an ultrafast ∼0.3 ps conversion of the SLE to SG that then evolves by ∼3 ps into the SE has been proposed to account for the collective deactivation character of d(AT)10. This presents a novel excited-state picture that can unify the seemingly conflicting time-resolved results reported previously for related AT DNAs. The direct spectral and dynamical data provided here contributes important photophysical parameters for the description of the excited states of AT oligomers. The possible connection between the energy transfer giving the SE and the photostability vs photodamage of A/T DNAs is briefly discussed.

# Nucleolus-Targeted Red Emissive Carbon Dots with Polarity-Sensitive and Excitation-Independent Fluorescence Emission: High-Resolution Cell Imaging and in Vivo Tracking\_2019

In this study, a new emulsifier precursor was prepared via esterification of avermectin with succinic anhydride. The chemical structure of the product was confirmed to be monosubstituted avermectin. After neutralization with triethanolamine, it exhibited adequate emulsification ability for avermectin. Avermectin was then encapsulated in nanoparticles in the nanoemulsion with a high drug loading up to 60 wt % and high stability. The nanoemulsion of nanoparticles that serves as a carrier of avermectin shows highly efficient pesticide characteristics, including low surface tension, high affinity to leaves, and improved photostability. In the presence of esterase or under strongly basic conditions, the ester bonds of the emulsifier can be hydrolyzed, and the encapsulated avermectin molecules can be released in an accelerated manner. The nanoemulsion exhibited improved insecticidal effect compared with commercial emulsifiable concentrate, which was attributed to the cleavage of ester bonds of the emulsifier by esterase in vivo.

# “Bright” and “Dark” Excited States of an Alternating AT Oligomer Characterized by Femtosecond Broadband Spectroscopy\_2009

Carbon dots (CDs) synthesized from biological sources have attracted much interest in bioimaging and biomedical applications due to their excellent biocompatibility, and thus, a facile synthesis of CDs with high fluorescence quantum yield (QY) is requisite for practical applications. In this work, we report a simple, rapid, and green approach to synthesize photoluminescent CDs using eutrophic algal blooms as the carbon source. This method offers a possibility for large scale production of highly luminescent CDs (QY = 13%) with the average particle size ∼8 nm. These CDs are highly water-soluble and exhibit nanosecond fluorescence lifetime with high photostability, luminescence stability in different environments, low cytotoxicity, and excellent cell permeability. Laser scanning confocal microscopy shows the uptake of CDs by MCF-7 cells, and the destined application of these CDs as a potential biomarker is demonstrated.

# Fabrication of an Effective Avermectin Nanoemulsion Using a Cleavable Succinic Ester Emulsifier\_2018

A new boron–dipyrromethene-based lysosome tracker, Lyso-NIR, is facilely synthesized. Besides the intensive near-infrared (NIR) fluorescence and high photostability, Lyso-NIR shows the capability to stably localize in lysosomes, which is independent of the local pH. Lyso-NIR does not have the problematic alkalization effect suffered by the commonly used lysotrackers; thus, it shows ignorable cytotoxicity and slightly affects normal physiological functions of lysosomes. The above advantages of Lyso-NIR make it feasible to track lysosomes’ dynamic changes in a relatively long time during the full cellular processes such as apoptosis, heavy metal stimulation, and endocytosis, as is demonstrated in this work. Moreover, Lyso-NIR’s narrow NIR emission at 740 nm with a full width at half-maximum smaller than 50 nm makes it easy to avoid the crosstalk with the emissions from other common fluorescent probes, which strengthens Lyso-NIR’s competitiveness as a standard lysosome tracker for multicolor bioimaging.

# Outright Green Synthesis of Fluorescent Carbon Dots from Eutrophic Algal Blooms for In Vitro Imaging\_2016

Semiconducting polymer dots (P-dots) recently have emerged as a new type of ultrabright fluorescent probe with promising applications in biological imaging and detection. With the increasing desire for near-infrared (NIR) fluorescing probes for in vivo biological measurements, the currently available NIR-emitting P-dots are very limited and the leaching of the encapsulated dyes/polymers has usually been a concern. To address this challenge, we first embedded the NIR dyes into the matrix of poly[(9,9-dioctylfluorene)-co-2,1,3-benzothiadiazole-co-4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole] (PF-BT-DBT) polymer and then enclosed the doped P-dots with polydiacetylenes (PDAs) to avoid potential leakage of the entrapped NIR dyes from the P-dot matrix. These PDA-enclosed NIR-emitting P-dots not only emitted much stronger NIR fluorescence than conventional organic molecules but also exhibited enhanced photostability over CdTe quantum dots, free NIR dyes, and gold nanoclusters. We next conjugated biomolecules onto the surface of the resulting P-dots and demonstrated their capability for specific cellular labeling without any noticeable nonspecific binding. To employ this new class of material as a facile sensing platform, an easy-to-prepare test paper, obtained by soaking the paper into the PDA-enclosed NIR-emitting P-dot solution, was used to sense external stimuli such as ions, temperature, or pH, depending on the surface functionalization of PDAs. We believe these PDA-coated NIR-fluorescing P-dots will be very useful in a variety of bioimaging and analytical applications.

# A Photostable Near-Infrared Fluorescent Tracker with pH-Independent Specificity to Lysosomes for Long Time and Multicolor Imaging\_2014

The photostability of polymeric materials is crucial for their applicability, especially under potentially harsh environmental conditions. In the current study, the influence of methyl-substitution on the photochemical stability of photoinitiator-derived benzoyl end groups is systematically investigated by a combination of pulsed-laser polymerization and subsequent size exclusion chromatography coupled with electrospray ionization mass spectrometry (PLP–SEC–ESI–MS), chemically induced dynamic nuclear polarization–nuclear magnetic resonance spectroscopy (CIDNP–NMR), and density functional theory (DFT) calculations. Poly(methyl methacrylate)s (pMMA) were synthesized employing benzoin-type photoinitiators with systematically substituted benzoyl moieties (i.e., 2-methylbenzoin, 3-methylbenzoin, 4-methylbenzoin, 2,4-dimethylbenzoin, 2,6-dimethylbenzoin, 2,4,6-trimethylbenzoin, 2,3,5,6-tetramethylbenzoin, and 2,3,4,5,6-pentamethylbenzoin). Photoinduced cleavage of the photoinitiator-based end group (irradiation at 351 and 355 nm) occurs solely for polymeric species with benzoyl end groups carrying no or only one ortho-methyl substituent/s, whereas all of the other substitution patterns lead to stable chain termini. The theoretical calculations suggest that the different reactivity can be traced back to shifts of the n−π\* transitions by approximately +0.25 eV. The current investigation unambiguously evidences that methylation in both ortho-positions of the benzoin-type photoinitiator critically enhances the photostability of the resulting polymer chain termini providing a clear instruction for photoinitiator design leading to polymers with stable chain termini.

# Polydiacetylene-Enclosed Near-Infrared Fluorescent Semiconducting Polymer Dots for Bioimaging and Sensing\_2014

Human carboxylesterase-2 (CE2) is a carboxylesterase that catalyzes the hydrolysis of endogenous and exogenous substrates. Abnormal CE2 levels are associated with various cancers, and CE2 is a key mediator of anticancer prodrugs, including irinotecan. Here, we developed a two-photon ratiometric probe for detecting CE2 activity using succinate ester as a recognition site for CE2. The probe showed high selectivity to CE2, a clear emission color change, high photostability, and bright two-photon microscopy (TPM) imaging capability, allowing the quantitative detection of CE2 activity in live cells. Using TPM ratio analysis, we show for the first time that CE2 activity was much lower in breast cancer cells than in normal cells. In CE2 overexpression studies, cancer cells had a markedly enhanced sensitivity to the cytotoxic effect of irinotecan, corresponding well with the TPM ratio of the probe. These results may provide useful information for quantitatively measuring CE2 activity in situ and predicting the responsiveness to anticancer drugs.

# Systematic Assessment of the Photochemical Stability of Photoinitiator-Derived Macromolecular Chain Termini\_2015

Novel near-infrared luminescent compounds based on platinum(II) 4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine-fused chlorins are described. These compounds have high photostability and display light emission, in particular simultaneous fluorescence and phosphorescence emission in solution at room temperature, in the biologically relevant 700–850 nm red and near-infrared (NIR) spectral region, making them excellent materials for biological imaging. The simultaneous presence of fluorescence and phosphorescence emission at room temperature, with the phosphorescence strongly quenched by oxygen whereas fluorescence remains unaffected, allows these compounds to be used as ratiometric oxygen sensors in chemical and biological media. Both steady-state (fluorescence vs phosphorescence intensities) and dynamic (dependence of phosphorescence lifetimes upon oxygen concentration) luminescence approaches can be used. Photocytotoxicity studies against human melanocytic melanoma cells (A375) indicate that these compounds display potential as photosensitizers in photodynamic therapy.

# Carboxylesterase-2-Selective Two-Photon Ratiometric Probe Reveals Decreased Carboxylesterase-2 Activity in Breast Cancer Cells\_2018

Colloidal semiconductor nanocrystals have gained substantial interest as spectrally tunable and bright fluorophores for color conversion and enrichment solids. However, they suffer from limitations in processing their solutions as well as efficiency degradation in solid films. As a remedy, embedding them into crystalline host matrixes has stepped forward for superior photostability, thermal stability, and chemical durability while simultaneously sustaining high quantum yields. Here, we review three basic methods for loading the macrocrystals with nanocrystals, namely relatively slow direct embedding, as well as accelerated methods of vacuum-assisted and liquid–liquid diffusion-assisted crystallization. We discuss photophysical properties of the resulting composites and present their application in light-emitting diodes as well as their utilization for plasmonics and excitonics. Finally, we present a future outlook for the science and technology of these materials.

# Colloidal Nanocrystals Embedded in Macrocrystals: Methods and Applications\_2016

A highly bright and photostable, fluorescent nanohybrid particle is presented which consists of gold nanoparticles (GNPs) embedded in dye-doped silica in a core–shell configuration. The dye used is the near-infrared emitting 4,5-benzo-5′-(iodoacetaminomethyl)-1′,3,3,3′,3′-pentamethyl-1-(4-sulfobutyl) indodicarbo cyanine. The nanohybrid architecture comprises a GNP core which is separated from a layer of dye molecules by a 15 nm buffer layer and has an outer protective, undoped silica shell. Using this architecture, a brightness factor of 550 has been achieved compared to the free dye. This hybrid system, referred to as Noble metal Enhanced Optical Nanohybrid (NEON) in this paper, is the first nanohybrid construct to our knowledge which demonstrates such tunable fluorescence property. NEON has enhanced photostability compared to the free dye and compared to a control particle without GNPs. Furthermore, the NEON particle, when used as a fluorescent label in a model bioassay, shows improved performance over assays using a conventional single dye molecule label.

# Platinum(II) Ring-Fused Chlorins as Near-Infrared Emitting Oxygen Sensors and Photodynamic Agents\_2017

Fluorescent dyes have enabled much progress in the broad range of biomedical fields. However, many commercially available dyes suffer from small Stokes shifts, resulting in poor signal-to-noise ratio and self-quenching on current microscope configurations. In this work, we have developed a general method to significantly increase the Stokes shifts of common fluorophores. By simply appending a 1,4-diethyl-decahydro-quinoxaline (DQ) moiety onto the conjugated structure, we introduced a vibronic backbone that could facilely expand the Stokes shifts, emission wavelength, and photostability of 11 different fluorophores by more than 3-fold. This generalizable method could significantly improve the imaging efficiency of commercial fluorophores. As a demonstration, we showed that the DQ derivative of hemicyanine generated 5-fold signal in mouse models over indocyanine green. Furthermore, the DQ-modified fluorophores could pair with their parent molecules to conduct one-excitation, multiple emission imaging, allowing us to study the cell behavior more robustly. This approach shows promise in generating dyes suitable for super-resolution microscopy and second window near-infrared imaging.

# Synthesis and Characterization of a Noble Metal Enhanced Optical Nanohybrid (NEON): A High Brightness Detection Platform Based on a Dye-Doped Silica Nanoparticle\_2012

Highly bright fluorescent gold nanoclusters (Au NCs) have been prepared by one-step reduction of aqueous precursor solution in the presence of multidentate thioether-terminated poly(methacrylic acid) (PTMP-PMAA). The fluorescence quantum yield of the resultant Au NCs is 4.8% higher than that of the similarly sized Au NCs prepared by the etching method (1.8–4.0%). These Au NCs show excellent photostability and have been successfully applied to label the hematopoietic cells first. The results show that Au NCs were endocytosed by the cancer cells significantly more than the normal cells, in comparison with control experiments labeled with fluorescent quantum dots (CdTe). The cytotoxicity experiments demonstrate the excellent biocompatibility of Au NCs, proven by a relatively lower cytotoxicity than CdTe. These robust near-infrared Au NCs show great potential in biolabeling, tracking, and imaging of other cells and diseases, especially in the diagnosis and treatment of chronic myeloid leukemia.

# A General Method To Increase Stokes Shift by Introducing Alternating Vibronic Structures\_2018

The IR780 iodide (IR780) is recognized as an effective theranostic agent for simultaneous near-infrared fluorescence imaging and photothermal therapy (PTT). However, the rigid chloro-cyclohexenyl ring makes IR780 insoluble in almost all pharmaceutically acceptable solvents, which inevitably limits its clinical application. We report folic acid (FA)-functionalized graphene quantum dots (GQDs-FA) containing a large and intact sp2 domain with carboxyl groups around the edge. Such GQDs-FA possess exceptionally high loading capacity for IR780 via strong π–π stacking interactions, and the water solubility of IR780 is improved by over 2400-fold after loading onto GQDs-FA (IR780/GQDs-FA). IR780/GQDs-FA with an improved photostability, an enhanced tumor-targeting ability, and a high photothermal conversion efficiency of 87.9% were capable of producing sufficient hyperthermia to effectively kill cancer cells and completely eradicate tumors upon 808 nm laser irradiation. The present IR780/GQDs-FA may open up great opportunities for the effective PTT to treat cancer.

# Biolabeling Hematopoietic System Cells Using Near-Infrared Fluorescent Gold Nanoclusters\_2011

Graphene quantum dots (GQDs) hold great promise as a new class of fluorophores for bioimaging, owing to their remarkable physicochemical properties including tunable photoluminescence, excellent photostability, and biocompatibility. Despite their highly anticipated potentials, GQDs have yet to be used to specifically label and track molecular targets involved in dynamic cellular processes in live cells. Here, we demonstrate that GQDs can serve as universal fluorophores for bioimaging because they can be readily conjugated with a wide range of biomolecules while preserving their functionalities. As a proof-of-concept demonstration, insulin-conjugated GQDs have been synthesized and utilized for specific labeling and dynamic tracking of insulin receptors in 3T3-L1 adipocytes. Our experiments reveal, for the first time, that the internalization and recycling of insulin receptors in adipocytes are oppositely regulated by apelin and TNFα, which may contribute to the regulations of these two cytokines in insulin sensitivity.

# Exceptionally High Payload of the IR780 Iodide on Folic Acid-Functionalized Graphene Quantum Dots for Targeted Photothermal Therapy\_2017

A novel organic sensitizer (AP3) with dual donors and dual anchor-acceptors based on an electron deficient thieno[3,4-b]pyrazine (TPz) π-bridge was synthesized, which shows an impressively high Jsc of 17.6 mA/cm2 when cosensitized with D35 (12.4 mA/cm2 as a single dye). Device power conversion efficiencies were observed at 7.5% under full sun intensity and in excess of 10% under reduced sun intensity. This novel dye design approach allows for devices showing photostability beyond 500 h for continuous irradiation and a tunable dye structure with an incident power conversion efficiency breadth reaching 800 nm from a simple-to-synthesize organic dye. Dye characterization with cyclic voltammetry, solution and film absorption, and computational analysis are all presented. Additionally, device characterization was performed through IV curves, IPCE, electron lifetime measurements, transient absorption spectroscopy, and current dynamic measurements at varying sun intensities to better understand the origin of the high device power conversion efficiencies as well as the interactions of AP3 and D35 in DSC devices.

# Graphene Quantum Dots as Universal Fluorophores and Their Use in Revealing Regulated Trafficking of Insulin Receptors in Adipocytes\_2013

Incorporation of guest materials inside single-crystalline hosts leads to single-crystal composites that have become more and more frequently seen in both biogenic and synthetic crystals. The unique composite structure together with long-range ordering promises special properties that are, however, less often demonstrated. Here, we examine the fluorescent properties of quantum dots (QDs) and polymer dots (Pdots) encapsulated inside the hosts of calcite single-crystals. Two CdTe QDs and two Pdots are incorporated into growing calcite crystals, as the QDs and Pdots are dispersed in the crystallization media of agarose gels. As a result, enhanced fluorescent properties are obtained from the QDs and Pdots inside calcite single-crystals with greatly improved photostability and significantly prolonged fluorescence lifetime, compared to those in solutions and gels. Particularly, the fluorescence lifetime increases by 0.5–1.6 times after the QDs or Pdots are incorporated. The enhanced fluorescent properties indicate the advantages of encapsulation by single-crystal hosts that provide dense shells to isolate the fluorescent nanoparticles from atmosphere. As such, this work has implications for advancing the research of single-crystal composites toward their functional design.

# A Stable Panchromatic Green Dual Acceptor, Dual Donor Organic Dye for Dye-Sensitized Solar Cells\_2017

Intelligent photoresponsive materials have shown broad applications in antiflake, coating, biomarker, information storage, and optical devices. This article describes the design and fabrication of a photoresponsive switch via a two-step procedure: (i) spiropyran (SP) as a chromophore was encapsulated within a block copolymer (poly(tert-butyl acrylate-co-ethyl acrylate-co-methacrylic acid), PTBEM) to produce SP@PTBEM micelle; (ii) an organic–inorganic ultrathin film (UTF) was prepared by layer-by-layer (LBL) self-assembly of the negatively charged SP@PTBEM micelle and positively charged MgAl-layered double hydroxide (LDH) nanoplatelets (denoted as (SP@PTBEM/LDHs)n UTF; n represents the bilayer number). Fluorescence spectroscopy and scanning electron microscopy (SEM) indicate a uniform and ordered layered structure with stepwise growth. The resulting (SP@PTBEM/LDHs)n UTF serves as an intelligent photoresponsive switch based on the structural transformation between SP and merocyanine (MC), which is triggered by alternate irradiation of UV/visible light. In addition, the UTF exhibits a high reversibility and photostability, which can be potentially used in photochromic materials and devices.

# Nanoparticles Incorporated inside Single-Crystals: Enhanced Fluorescent Properties\_2016

CdSe and CdTe nanocrystals are linked to nanostructured TiO2 films using 3-mercaptopropionic acid as a linker molecule for establishing the mechanistic aspects of interfacial charge transfer processes. Both these quantum dots are energetically capable of sensitizing TiO2 films and generating photocurrents in quantum dot solar cells. These two semiconductor nanocrystals exhibit markedly different external quantum efficiencies (∼70% for CdSe and ∼0.1% for CdTe at 555 nm). Although CdTe with a more favorable conduction band energy (ECB = −1.0 V vs NHE) is capable of injecting electrons into TiO2 faster than CdSe (ECB = −0.6 V vs NHE), hole scavenging by a sulfide redox couple remains a major bottleneck. The sulfide ions dissolved in aqueous solutions are capable of scavenging photogenerated holes in photoirradiated CdSe system but not in CdTe. The anodic corrosion and exchange of Te with S dominate the charge transfer at the CdTe interface. Factors that dictate the efficiency and photostability of CdSe and CdTe quantum dots are discussed.

# A Light-Triggered Switch Based on Spiropyran/Layered Double Hydroxide Ultrathin Films\_2015

Malignant tumor incidences have been rapidly rising recently and are becoming a serious threat to human health. Herein, a multifunctional cancer targeted theranostic nanoplatform is developed by in situ growth of iron oxide magnetic nanoparticles on carbon nanoparticles, and then loaded with fluorescent dye indocyanine green (ICG@MCNPs). The loading of ICG on the nanoplatform significantly improves its photostability, and hence facilitates long-term near-infrared fluorescence (NIRF) imaging and efficient photothermal therapy (PTT) of tumor. The in vivo NIRF imaging reveals that ICG@MCNPs can be targeted to the tumor site. Moreover, in vivo magnetic resonance imaging also confirmed the efficient accumulation of ICG@MCNPs in the tumor site. Inspiringly, the subsequent PTT of tumor-bearing mice is achieved, as evidenced by the complete ablation of the tumor and the recovery of the physiological indexes to normal levels. Benefitting from its low-cost, simple preparation, and excellent dual-modal imaging and therapy, the ICG@MCNPs-based theranostic nanoplatform holds great promise in tumor-targeted nanomedicine.

# Quantum Dot Sensitized Solar Cells. A Tale of Two Semiconductor Nanocrystals: CdSe and CdTe\_2009

Photobleaching and photostability of proteins of the green fluorescent protein (GFP) family are crucially important for practical applications of these widely used biomarkers. On the basis of simulations, we propose a mechanism for irreversible bleaching in GFP-type proteins under intense light illumination. The key feature of the mechanism is a photoinduced reaction of the chromophore with molecular oxygen (O2) inside the protein barrel leading to the chromophore’s decomposition. Using quantum mechanics/molecular mechanics (QM/MM) modeling we show that a model system comprising the protein-bound Chro– and O2 can be excited to an electronic state of the intermolecular charge-transfer (CT) character (Chro•···O2–•). Once in the CT state, the system undergoes a series of chemical reactions with low activation barriers resulting in the cleavage of the bridging bond between the phenolic and imidazolinone rings and disintegration of the chromophore.

# Indocyanine Green Loaded Magnetic Carbon Nanoparticles for Near Infrared Fluorescence/Magnetic Resonance Dual-Modal Imaging and Photothermal Therapy of Tumor\_2017

Mimicking the green fluorescent protein (GFP), multicolor fluorescent polymers possessing enhanced fluorescence have been developed and applied to single-excitation cell imaging. The GFP core chromophore was covalently linked to the azide-functionalized amphiphilic block polymer poly(ethylene glycol)–azide–poly(methyl methacrylate). Through macromolecular assembly into micelles, the fluorescence enhanced and further increased with the elongation of poly(methyl methacrylate) chain due to the segmentation effect of the polymeric framework, which could reduce strong π–π interaction and suppress the chromophore’s conformational motion. By a combination of chemically tailoring the core chromophore and macromolecular assembly strategy, multicolor fluorescent polymers showing a color palette from blue to orange were achieved under similar excitation conditions with the highest emission quantum yield approaching 8%, which is more than 80-fold larger than that of the core chromophore. Moreover, fluorescent emission color could be regulated by tuning the coassembling constitution of green and orange fluorescent polymers, generating three new types of emission color. Owing to their low cytotoxicity and good photostability, GFP-mimicking fluorescent polymers were suitable for single-excitation multicolor cell imaging, exhibiting maximum Stokes shift of 202 nm, ascribing to the effect of excited-state proton transfer (ESPT). More importantly, green, yellow, and orange fluorescent cell images were obtained from one single visual field, demonstrating identical information on examined cells, which would improve the accuracy and reliability of biological analysis.

# A Light-Induced Reaction with Oxygen Leads to Chromophore Decomposition and Irreversible Photobleaching in GFP-Type Proteins\_2015

In recent years, metal-enhanced fluorescence (MEF) using silver particles has been reported for a number of fluorophores emitting at visible wavelengths. However, it was generally thought that silver particles would always quench fluorescence at shorter wavelengths. We now report the observation of MEF of the tryptophan analogue N-acetyl-l-tryptophanamide (NATA) on silver nanostructured surfaces. NATA is a model for the intrinsic tryptophan emission from proteins. We have also studied the effects of silver nanostructures on the emission of N-acetyl-l-tyrosinamide (NATA-tyr). In the case of NATA, we observed increased emission, decrease in fluorescence lifetimes, and increase in photostability when NATA was embedded in 15 nm thick spin-casted poly(vinyl alcohol) film on silver nanostructured surfaces. We have also investigated the effects of silver nanostructures on the emission from thin poly(vinyl alcohol) films containing NATA-tyr. However, we observed no increase in fluorescence signal for NATA-tyr on silver nanostructures. To understand these results, we performed numerical calculations using the finite-difference time-domain (FDTD) technique to model a tryptophan-wavelength dipole near a spherical silver particle. Our calculations reveal an enhancement of the power of the radiated emission by the excited-state fluorophore in proximity to a 100 nm diameter silver nanoparticle covering the emission spectra of NATA and NATA-tyr. These calculations show a clear wavelength dependence with the specific spectral region displaying low-enhancement at the shorter NATA-tyr wavelength and higher enhancement at NATA emission wavelength. Our FDTD calculations also reveal that excited fluorophores in the near-field of a 100 nm silver nanoparticle can induce enhancement fields of varying degrees of the intensity of the near-fields around the particle that is dependent on the wavelength of the emission. We believe these enhanced near-fields play a role in our observation of MEF from metal surfaces. The enhanced emission of NATA on silver nanostructures suggests that the extension of MEF to the UV region opens new possibilities to study tryptophan-containing proteins without labeling with longer wavelength fluorophores, leading to label-free detection of biomolecules.

# Multicolor Fluorescent Polymers Inspired from Green Fluorescent Protein\_2015

An anionic conjugated polyelectrolyte (CPE, P1) with energy donor−acceptor architecture is synthesized and assembled with an Arg-Gly-Asp (RGD) terminated peptide to form fluorescent nanoparticles (FNs) with targeting capability. Complexation between oppositely charged P1 and the peptide at different molar ratio results in FNs with different size and fluorescence varying from sky-blue to orange-red because of aggregation-enhanced fluorescence resonance energy transfer (FRET). At the P1/peptide molar ratio of 8:0.9, the FNs exhibit bright orange-red fluorescence with a quantum yield of 16% and a large Stokes shift of 195 nm. In addition, these FNs also possess low cytotoxicity and good photostability. By virtue of the specific binding between RGD and integrin receptors, the P1/peptide FNs serve as an effective probe for receptor-targeted fluorescence imaging of HT29 cancer cells. This study thus provides a facile and generic strategy to prepare a new generation of multicolor polymeric FNs with native targeting capability and controllable properties for biological applications.

# Metal-Enhanced Intrinsic Fluorescence of Proteins on Silver Nanostructured Surfaces toward Label-Free Detection\_2008

We have synthesized the unnatural amino acid (UAA), 4-azidomethyl-l-phenylalanine (pN3CH2Phe), to serve as an effective vibrational reporter of local protein environments. The position, extinction coefficient, and sensitivity to local environment of the azide asymmetric stretch vibration of pN3CH2Phe are compared to the vibrational reporters: 4-cyano-l-phenylalanine (pCNPhe) and 4-azido-l-phenylalanine (pN3Phe). This UAA was genetically incorporated in a site-specific manner utilizing an engineered, orthogonal aminoacyl-tRNA synthetase in response to an amber codon with high efficiency and fidelity into two distinct sites in superfolder green fluorescent protein (sfGFP). This allowed for the dependence of the azide asymmetric stretch vibration of pN3CH2Phe to different protein environments to be measured. The photostability of pN3CH2Phe was also measured relative to the photoreactive UAA, pN3Phe.

# Multicolor Conjugate Polyelectrolyte/Peptide Complexes as Self-Assembled Nanoparticles for Receptor-Targeted Cellular Imaging\_2010

A highly efficient quantum dot (QD)/inorganic layer/dye molecule sandwich structure was designed and applied in electrochemical QD-sensitized solar cells. The key component TiO2/CdS/ZnS/N719 hybrid photoanode with ZnS insertion between the two types of sensitizers was demonstrated not only to efficiently extend the light absorption but also to suppress the charge recombination from either TiO2 or CdS QDs to electrolyte redox species, yielding a photocurrent density of 11.04 mA cm–2, an open-circuit voltage of 713 mV, a fill factor of 0.559, and an impressive overall energy conversion efficiency of 4.4%. More importantly, the cell exhibited enhanced photostability with the help of the synergistic stabilizing effect of both the organic and the inorganic passivation layers in the presence of a corrosive electrolyte.

# Sensitive, Site-Specific, and Stable Vibrational Probe of Local Protein Environments: 4-Azidomethyl-l-Phenylalanine\_2013

The behavior of a fluorophore near a gold nanoparticle is rationalized by a theoretical description of the parameters that modify the fluorescence emission: nanoparticle–fluorophore distance, fluorescence quantum yield (ϕ0), and fluorophore absorption and emission spectra, to find optimum conditions for designing fluorophore–nanoparticle probes. The theoretical maximum gain in brightness of the nanoparticle–fluorophore system with respect to the isolated molecule increases almost inversely proportional to ϕ0. The brightness enhancement in imaging experiments in vitro was assessed by using Au-SiO2 core–shell nanoparticles deposited on glass. A ∼13-fold emission brightness enhancement for weakly fluorescent molecules was observed. A significant increase in fluorophore photostability, rendering longer imaging times, was obtained for fluorophores interacting with gold nanoparticles incorporated by endocytosis in cells. Our results illustrate a way to increase imaging times and to study molecules in the vicinity of a metallic nanoparticle after photobleaching of background fluorescence.

# Study of Quantum Dot/Inorganic Layer/Dye Molecule Sandwich Structure for Electrochemical Solar Cells\_2012

We have investigated electronic excitation energy transfer in a specifically designed bichromophoric donor/acceptor dyad in which the donor (perylenediimide) and acceptor (terrylenediimide) are linked by a rigid heptaphenyl-spacer. Because of the choice of the bridge, which defines the distance and orientation of the two chromophores, donor as well as acceptor emission is observed. The significantly smaller photostability of the donor allows for time-resolved measurements of the acceptor emission at the single-molecule level with and without energy transfer from the donor. By analyzing the differences of the rise/decay profiles for both pathways, we could determine time constants of energy transfer with high accuracy for single dyads. The results show that the experimental approach presented here works even for situations in which the energy transfer times are smaller than the temporal resolution of the detection system.

# Detection of Low Quantum Yield Fluorophores and Improved Imaging Times Using Metallic Nanoparticles\_2012

In recent years, Ge nanomaterials have aroused a great deal of attention because of their unique physical and chemical properties. However, the current synthesis methods bear some disadvantages, such as high reaction temperature, dangerous reagents, and inert atmospheres. In this paper, we developed a facile one-step route for preparing fluorescent and water-dispersed germanium nanoparticles (Ge NPs) by utilizing organogermanes as the precursor, operated at mild reactive conditions. The as-synthesized Ge NPs have an average diameter of 2.6 ± 0.5 nm and intense blue-green fluorescence (FL). Furthermore, the as-synthesized Ge NPs show remarkable water dispersibility, favorable biocompatibility, outstanding photostability, excellent storage stability, and low cytotoxicity. More importantly, these Ge NPs can act as a satisfactory FL probe and successfully be applied to cellular imaging of HeLa. The present study offers a simple and moderate strategy for the preparation of Ge NPs and expedites Ge NPs for bioimaging applications.

# Time-Resolved Measurements of Intramolecular Energy Transfer in Single Donor/Acceptor Dyads\_2005

We prepared a new conjugated polymer nanoparticle with the size of about 50 nm that is prepared by electrostatic assembly of cationic conjugated polymer PFO and anionic poly(l-glutamic acid) conjugated with anticancer drug doxorubicin (PFO/PG-Dox). The PFO exhibits good fluorescence quantum yield, photostability, and little cytotoxicity to meet the essential requests for cell imaging. In PFO/PG-Dox nanoparticles, the fluorescence of PFO is highly quenched by Dox by electron transfer mechanism, and thus the PFO is in the fluorescence “turn-off’ state. After PFO/PG-Dox nanoparticles are exposed to carboxypeptidase or are taken up by cancer cells, the poly(l-glutamic acid) is hydrolysed to release the Dox, inducing the activation of PFO fluorescence to “turn-on” state. This multifunctional nanoparticle system can deliver Dox to targeted cancer cells and monitor the Dox release based on fluorescence “turn-on” signal of PFO, which concurrently images the cancer cells. The present work opens the door for new functional studies of conjugated polymer in simultaneous imaging and disease therapeutics.

# Synthesis of Fluorescent and Water-Dispersed Germanium Nanoparticles and Their Cellular Imaging Applications\_2018

This study reports the preparation of functional bioinorganic hybrid materials exhibiting catalytic activity and photoluminescent properties arising from the combination of enzymes and freestanding silicon-based nanoparticles. The hybrid materials reported herein have potential applications in biological sensing/imaging and theranostics, as they combine long-lived silicon-based nanoparticle photoluminescence with substrate-specific enzymatic activity. Thermal hydrosilylation of undecenoic acid and alkene-terminated poly(ethylene oxide) with hydride-terminated silicon nanocrystals afforded nanoparticles functionalized with a mixed surface made up of carboxylic acid and poly(ethylene oxide) moieties. These silicon-based nanoparticles were subsequently conjugated with prototypical enzymes through the carbodiimide-mediated amide coupling reaction in order to form bioinorganic hybrids that display solubility and photostability in phosphate buffer, photoluminescence (λmax = 630 nm), and enzymatic activity. They were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), dynamic light scattering analysis (DLS), photoluminescence spectroscopy, and pertinent enzyme activity assays.

# Conjugated Polymer Nanoparticles for Drug Delivery and Imaging\_2010

Aurintricarboxylic acid (ATA), a UV absorbent, has successfully been intercalated into the interlayer spacing of Zn–Al–NO3-LDHs precursor through an anion-exchange reaction. The structure and the thermal- and photostability of the intercalated product were investigated by various techniques such as powder X-ray diffraction (XRD), infrared spectroscopy (FT-IR), thermogravimetry and differential thermal analysis (TG–DTA), and UV–vis spectroscopy. The increase of the basal spacing from 0.90 to 1.52 nm as observed by XRD suggests that the ATA anions have replaced the NO3– anions in the interlayer region of the precursor LDHs. The results of infrared spectroscopy and thermogravimetry and differential thermal analysis (TG–DTA) also reveal the presence of supramolecular host–guest interactions between the brucite-like sheet and the intercalated ATA anions. The intercalation of the ATA anions into the LDHs markedly enhances the thermal stability of this UV absorbent. After incorporation of 1 wt % ZnAl-ATA-LDHs to polypropylene (PP), also, the resulted ZnAl-ATA-LDHs/PP composite has much higher resistance to UV degradation related to PP.

# Functional Bioinorganic Hybrids from Enzymes and Luminescent Silicon-Based Nanoparticles\_2018

The fluorescence method has made great progress in the construction of sensitive sensors but the background fluorescence of the matrix and photobleaching limit its broad application in clinical diagnosis. Here, we propose a digital single virus immunoassay for multiplex virus detection by using fluorescent magnetic multifunctional nanospheres as both capture carriers and signal labels. The superparamagnetism and strong magnetic response ability of nanospheres can realize efficient capture and separation of targets without sample pretreatment. Due to their distinguishable fluorescence imaging and photostability, the nanospheres enable single-particle counting for ultrasensitive multiplexed detection. Furthermore, the integration of digital analysis provided a reliable quantitative strategy for the detection of rare targets. Based on multifunctional nanospheres and digital analysis, a digital single virus immunoassay was proposed for simultaneous detection of H9N2, H1N1, and H7N9 avian influenza virus without complex signal amplification, whose detection limits were 0.02 pg/mL. Owing to its good specificity and anti-interference ability, the method showed great potential in single biomolecules, multiplexed detection, and early diagnosis of diseases.

# Synthesis and UV Absorption Properties of Aurintricarboxylic Acid Intercalated Zn–Al Layered Double Hydroxides\_2011

We have demonstrated that the subcellular targeting properties of the indole-based cyanines can be tuned by the functional substituent attached onto the indole moiety in which the first example of a highly RNA-selective and two-photon active fluorescent light-up probe for high contrast and brightness TPEF images of rRNA in the nucleolus of live cells has been developed. It is important to find that this cyanine binds much stronger toward RNA than DNA in a buffer solution as well as selectively stains and targets to rRNA in the nucleolus. Remarkably, the TPEF brightness (Φσmax) is dramatically increased with 11-fold enhancement in the presence of rRNA, leading to the record high Φσmax of 228 GM for RNA. This probe not only shows good biocompatibility and superior photostability but also offers general applicability to various live cell lines including HeLa, HepG2, MCF-7, and KB cells and excellent counterstaining compatibility with commercially available DNA or protein trackers.

# Digital Single Virus Immunoassay for Ultrasensitive Multiplex Avian Influenza Virus Detection Based on Fluorescent Magnetic Multifunctional Nanospheres\_2019

Direct arylation polymerization (DARP) is a novel approach to obtain conjugated polymers (CPs) through the straightforward C–H activation of monomer building blocks. In this work, a convenient DARP method with high efficiency and excellent regioselectivity is developed to synthesize a series of donor–acceptor (D–A)-type CPs composed of electron-acceptor moiety fluorenones (FOs) and various electron-donor moieties. CPs with different band gaps are obtained in good yields and display large Stokes shifts up to 295 nm. Two ionic CPs, PFOP-NEt3(+) and PFOP-COO(−), were prepared in a polar solvent system to improve the water solubility and biocompatibility using the proposed DARP method. Detailed photophysical studies of these two CPs suggest that both solvation and hydrogen bonds play important roles in determining the polymers’ spectroscopic properties. Further studies of the cationic polymer PFOP-NEt3(+) in cell imaging demonstrate its potential application in labeling cell membranes and lysosomes given its low cytotoxicity, excellent photostability, and specific subcellular localization.

# Indole-based Cyanine as a Nuclear RNA-Selective Two-Photon Fluorescent Probe for Live Cell Imaging\_2015

Hybrid bicelles have been demonstrated to have great potential for hydrophobic drug delivery. Herein, we report a near-infrared light-driven, temperature-sensitive hybrid bicelles co-encapsulating hydrophobic doxorubicin (DOX) and indocyanine green (ICG) (DOX/ICG@HBs). Encapsulation of ICG into the lipid bilayer membrane of DOX/ICG@HBs results in higher photostability than free ICG. DOX/ICG@HBs exhibited temperature-regulated drug release behavior and significant photothermal cytotoxicity. After tail vein injection, such discotic nanoparticles of DOX/ICG@HBs were found to accumulate selectively at the tumor site and act as an efficient probe to enhance fluorescence imaging greatly. The in vivo experiments showed that the DOX/ICG@HBs-mediated chemo- and photothermal combination therapy was more cytotoxic to tumor cells than the photothermal treatment or the chemotherapy alone due to the synergistic effect, reducing the occurrence of tumor metastasis. Therefore, DOX/ICG@HBs can act as a powerful nanotheranostic agent for chemo/photothermal therapy of cancer under the guidance of near-infrared fluorescence imaging.

# One-Step Construction of Fluorenone-Based Donor–Acceptor-Type Conjugated Polymers via Direct Arylation Polymerization for Cell-Imaging Applications\_2019

In recent years, fluorogens with aggregation-induced emission (AIE) characteristics have attracted considerable research interest in design and preparation of fluorescent organic nanoparticles (NPs) for bioimaging. So far, plenty of AIE NPs have been successfully utilized for in vitro and in vivo fluorescence imaging applications, which show outstanding performances by virtue of their unique advantages in terms of high brightness, excellent photostability, free of random blinking, facile cell internalization and superb cellular retention as well as negligible cytotoxicity and in vivo toxicity. In this chapter, the recent status of the development of AIE NPs for in vitro fluorescence imaging was summarized according to their utilizations, including non-specific cell imaging, targeted cancer cell imaging, specific organelle imaging, in vitro long-term cell tracking, and bacterial imaging. Furthermore, we also discuss the in vivo applications of AIE NPs in in vivo fluorescence imaging of tumors, intravital two-photon fluorescence imaging, in vivo long-term cell tracking as well as in vivo dual-modality imaging. The perspectives for the future investigation of advanced AIE NPs for bioimaging are discussed in this chapter as well.

# Doxorubicin and Indocyanine Green Loaded Hybrid Bicelles for Fluorescence Imaging Guided Synergetic Chemo/Photothermal Therapy\_2017

In situ detecting and monitoring intracellular telomerase activity is significant for cancer diagnosis. In this work, we report a facile and fast-responsive bioprobe for in situ detection and imaging of intracellular telomerase activity with superior photostability. After transfected into living cells, quencher group labeled TS primer (QP) can be extended in the presence of intracellular telomerase. Positive charged TPE-Py molecules (AIE dye) will bind to the primer as well as extension repeated units, producing a telomerase activity-related turn-on fluorescence signal. By incorporating positive charged AIE dye and substrate oligonucleotides, in situ light-up imaging and detection of intracellular telomerase activity were achieved. This strategy exhibits good performance for sensitive in situ tracking of telomerase activity in living cells. The practicality of this facile and fast-responsive telomerase detection method was demonstrated by using it to distinguish tumor cells from normal cells and to monitor the change of telomerase activity during treatment with antitumor drugs, which shows its potential in clinical diagnostic and therapeutic monitoring.

# AIE Nanoparticles for in Vitro and in Vivo Imaging\_2016

A polyphenylenevinylene derivative electroluminescent polymer was successfully incorporated into the channels of mesoporous silica SBA-15 with platelet morphology, and the obtained material was fully characterized by mean of X-ray diffraction, nitrogen physisorption porosimetry, infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM), solid-state nuclear magnetic resonance (SS-NMR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy and photoluminescence spectroscopy. The hybrid host–guest system displays significant pore size and volume restriction, along with luminescent properties that mimic those of the polymer in solution, as a consequence of strongly reduced aggregation of the polymer chains when confined in the SBA-15 channels. Moreover, the new composite material possesses a higher photostability than the pure polymer and represents a promising candidate for further use in the field of optoelectronic devices.

# Facile, Fast-Responsive, and Photostable Imaging of Telomerase Activity in Living Cells with a Fluorescence Turn-On Manner\_2016

Fluorescent polymeric nanoparticles (FPNs) as novel theranostic agents for cancer diagnosis and treatment have been widely investigated in recent years. However, most FPNs were constructed with typical inorganic quantum dots, fluorescent proteins, and conventional organic dyes, which have still suffered from many obstacles such as serious cytotoxicity, easy enzymolysis, and vicious aggregation-caused fluorescence quenching (ACQ). Herein, to overcome these problems, we design and synthesize novel FPNs with a unique aggregation-induced emission (AIE) feature using resourceful and cost-effective oxidized sodium alginate (OSA) as natural polymer protected shells of FPNs. Moreover, differing from commercial or synthetic polymers such as PEG, BSA, and lecithin, sodium alginate from marine seaweeds is a cheaper, abundant source and excellent has biocompatibility. Thus-prepared AIE-active OSA-Phe-OSA FPNs by the facile Schiff base condensation have many advantages, such as strong fluorescence, great water dispersity, excellent photostability and desirable biocompatibility, and stained performance. These features endow them great potential for various biomedical applications.

# Incorporation of a Semiconductive Polymer into Mesoporous SBA-15 Platelets: Toward New Luminescent Hybrid Materials\_2011

The development of fluorescent proteins (FPs) has revolutionized cell biology research. The monomeric variants of red fluorescent proteins (RFPs), known as mFruits, have been especially valuable for tagging and tracking cellular processes in vivo. Determining oxygen diffusion pathways in FPs can be important for improving photostability and for understanding maturation of the chromophore. We use molecular dynamics (MD) calculations to investigate the diffusion of molecular oxygen in one of the most useful monomeric RFPs, mCherry. We describe a pathway that allows oxygen molecules to enter from the solvent and travel through the protein barrel to the chromophore. We calculate the free-energy of an oxygen molecule at points along the path. The pathway contains several oxygen hosting pockets, which are identified by the amino acid residues that form the pocket. We also investigate an RFP variant known to be significantly less photostable than mCherry and find much easier oxygen access in this variant. The results provide a better understanding of the mechanism of molecular oxygen access into the fully folded mCherry protein barrel and provide insight into the photobleaching process in these proteins.

# Novel Strategy toward AIE-Active Fluorescent Polymeric Nanoparticles from Polysaccharides: Preparation and Cell Imaging\_2017

Polymer microfibers with a circular cross-section are directly drawn from a solution. By encapsulating the dye-doped microfibers with polydimethylsiloxane (PDMS) elastomer, optically pumped lasing with enhanced photostability is achieved. The lasing characteristics as well as size-dependent lasing action are carefully analyzed, and the lasing phenomenon is ascribed to whispering gallery mode. The PDMS elastomer offers another degree of freedom to mechanically tune the lasing from microfibers. It is interesting to note that by different types of bending, bidirectional shifting of the laser wavelength is observed, which is due to strain-induced refractive index change of the fiber and PDMS matrix. Our studies not only show an effective method to passivate the microfibers, but also open up a new approach to manipulating the lasing, which allows for fine adjustment of laser emission to any desired wavelength within the tuning range.

# Exploring the Diffusion of Molecular Oxygen in the Red Fluorescent Protein mCherry Using Explicit Oxygen Molecular Dynamics Simulations\_2013

Measuring the levels of Fe3+ in human body has attracted considerable attention for health monitoring as it plays an essential role in many physiological processes. In this work, we reported a selective fluorescent nanoprobe for Fe3+ detection in biological samples based on ultrabright N/P codoped carbon dots. By employing adenosine 5′-triphosphate (ATP) as the carbon, nitrogen, and phosphorus source, the N/P codoped carbon dots could be simply prepared through hydrothermal treatment. The obtained carbon dots exhibited high quantum yields up to 43.2%, as well as excellent photostability, low toxicity, and water solubility. Because of the Fe–O–P bonds formed between Fe3+ and the N/P codoped carbon dots, this nanoprobe showed high selectivity toward Fe3+ against various potential interfering substances in the presence of EDTA. The fluorescence quenching of as-fabricated carbon dots was observed with the increasing Fe3+ concentration, and the calibration curve displayed a wide linear region over the range of 1–150 μM with a detection limit of 0.33 μM. The satisfactory accuracy was further confirmed with the river samples and ferrous sulfate tablets, respectively. With the above outstanding properties, these N/P codoped carbon dots were successfully applied for direct detection of Fe3+ in biological samples including human blood serum and living cells. As compared to the most reported carbon dots-based Fe3+ sensors, this nanoprobe showed high fluorescence, good accuracy, and excellent selectivity, which presents the potential practical application for diagnosis of Fe3+ related disease.

# Bending-Induced Bidirectional Tuning of Whispering Gallery Mode Lasing from Flexible Polymer Fibers\_2014

2-Aminooxazole is generally considered a prebiotic precursor of ribonucleotides on the early earth. Its pentose compound, pentose aminooxazoline, has been suggested to be a key intermediate in the prebiotic synthetic scenario. In this article, detailed mechanism of the photochemistry of pentose aminooxazoline has been studied by performing density functional theory and multireference complete active space self-consistent field calculations. Parallel to the “ring-puckering” process, which leads to ultrafast nonradiative deactivation, several other photodissociation channels are explored in detail. In addition, the influences of the pentose structure and solvation effects with both implicit and explicit water models have been uncovered for both neutral and protonated forms. The current theoretical results provide very important information not only for the photostability of RNA nucleotides but also for an in-depth understanding of the synthesis of other prebiotic nucleotides.

# Highly Fe3+-Selective Fluorescent Nanoprobe Based on Ultrabright N/P Codoped Carbon Dots and Its Application in Biological Samples\_2017

Despite many efforts focused on the emission origin of carbon dots (CDs), it is still a topic of debate. This is mainly due to the complex structure of these nanomaterials. Here, we developed an innovative method to evaluate the number and spectral characterizations of various emission centers in CDs. We monitored the photostability of a series of column-separated CDs under UV irradiation to obtain three-dimensional data sets and resolve them using multivariate decomposition methods. The obtained results clearly revealed the presence of three different types of emission centers in CDs, including molecular states, aromatic domain states, and carbon-core states so that their single or coexisting appearance was found to be deeply dependent on the reaction temperature. Furthermore, density functional theory and time-dependent density functional theory were used to investigate the electronic and optical properties of some different aza-polycyclic and corannulene molecules as possible polycyclic aromatic hydrocarbons responsible for the above-mentioned aromatic domain states.

# Theoretical Studies on the Photochemistry of Pentose Aminooxazoline, a Hypothetical Intermediate Product in the Prebiotic Synthetic Scenario of RNA Nucleotides\_2016

Despite many efforts focused on the emission origin of carbon dots (CDs), it is still a topic of debate. This is mainly due to the complex structure of these nanomaterials. Here, we developed an innovative method to evaluate the number and spectral characterizations of various emission centers in CDs. We monitored the photostability of a series of column-separated CDs under UV irradiation to obtain three-dimensional data sets and resolve them using multivariate decomposition methods. The obtained results clearly revealed the presence of three different types of emission centers in CDs, including molecular states, aromatic domain states, and carbon-core states so that their single or coexisting appearance was found to be deeply dependent on the reaction temperature. Furthermore, density functional theory and time-dependent density functional theory were used to investigate the electronic and optical properties of some different aza-polycyclic and corannulene molecules as possible polycyclic aromatic hydrocarbons responsible for the above-mentioned aromatic domain states.

# Resolving the Multiple Emission Centers in Carbon Dots: From Fluorophore Molecular States to Aromatic Domain States and Carbon-Core States\_2018

Development of special organic materials that are able to absorb light energy in the second near-infrared window (NIR-II) is significantly important for treating deep-tissue-buried diseases or supplying power to implantable electronic devices. Herein, a narrow bandgap donor–acceptor (D-A) conjugated polymer with thiophene-fused benzodifurandione-based oligo(p-phenylenevinylene) (TBDOPV) as acceptor part and 2,2′-bithiophene (DT) as donor part was developed and exploited as a photothermal conversion material with high extinction coefficient and robust photostability in the NIR-II window. According to transient absorption analysis results, the photothermal conversion ability of this polymer is attributed to the fast internal conversion (IC) process. The high photothermal conversion efficiency makes this polymer a promising NIR-II adsorbing antenna to remotely actuate thermo-dependent devices, e.g., high-performance photothermal–electrical and photothermal–mechanical converters.

# Real-Time Monitoring of Dissolved Oxygen with Inherent Oxygen-Sensitive Centers in Metal–Organic Frameworks\_2016

A water-soluble zinc phthalocyanine (ZnPc) complex with four negatively charged electron-withdrawing sulfonic acid substituents at the nonperipheral positions (α-ZnTSPc) is found to have a high singlet oxygen (1O2) quantum yield and exhibits high photostability. The formation of aggregates is hindered and the highest occupied molecular orbital is significantly stabilized, making α-ZnTSPc potentially suitable for its use as a photosensitizer for photodynamic therapy and photoimmunotherapy. Atomic force microscopy (AFM) reveals that mixtures of the negatively charged α-ZnTSPc complex with a similar positively charged ZnPc were found to result in the self-assembly of one-dimensional accordion-like fibers. Supramolecular fibers can be formed in aqueous solutions through intermolecular electrostatic and donor–acceptor interactions between the two water-soluble ZnPcs.

# Self-Assembled Bilayers on Nanocrystalline Metal Oxides: Exploring the Non-Innocent Nature of the Linking Ions\_2017

2-Aminooxazole is generally considered a prebiotic precursor of ribonucleotides on the early earth. Its pentose compound, pentose aminooxazoline, has been suggested to be a key intermediate in the prebiotic synthetic scenario. In this article, detailed mechanism of the photochemistry of pentose aminooxazoline has been studied by performing density functional theory and multireference complete active space self-consistent field calculations. Parallel to the “ring-puckering” process, which leads to ultrafast nonradiative deactivation, several other photodissociation channels are explored in detail. In addition, the influences of the pentose structure and solvation effects with both implicit and explicit water models have been uncovered for both neutral and protonated forms. The current theoretical results provide very important information not only for the photostability of RNA nucleotides but also for an in-depth understanding of the synthesis of other prebiotic nucleotides.

# One-Pot To Synthesize Multifunctional Carbon Dots for Near Infrared Fluorescence Imaging and Photothermal Cancer Therapy\_2016

A simple and effective protocol for detections of protein−protein and protein−small molecule interactions has been developed. After interactions between proteins and their corresponding ligands, we employed colloidal silver staining for producing active substrates for surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence (SEF). Tetramethylrhodamine isothiocyanate (TRITC) and Atto610 were used for both Raman and fluorescent probes. We detected interactions between human IgG and TRITC−anti-human IgG, and those between avidin and Atto610-biotin by surface-enhanced resonance Raman scattering (SERRS) and SEF. The detection limits of the proposed SERRS-based method are comparable to those of the proposed SEF-based one, 0.9 pg/mL for anti-human IgG and 0.1 pg/mL for biotin. This protocol exploits several advantages of simplicity over other SERS and SEF-based related methods because of the protein staining-based strategy for silver nanoparticle assembling, high sensitivity from SERRS and SEF, and high stability in photostability comparing to fluorescence-based protein detections. Therefore, the proposed method for detection of protein−ligand interactions has great potential in high-sensitivity and high-throughput chip-based protein function determination.

# Simplified Protocol for Detection of Protein−Ligand Interactions via Surface-Enhanced Resonance Raman Scattering and Surface-Enhanced Fluorescence\_2008

Despite that they are regarded as the ideal sensory platform, there are still no reports on luminescent metal–organic frameworks (LMOFs) for dissolved oxygen (DO) measurement. Here, we reported the rational construction of a platinum(II) porphyrinic LMOF, PCN-224(Pt), as an novel porous matrix for the phosphorescent DO sensing with commercially available Pt(II) meso-tetra(4-carboxyphenyl)porphyrin as the bridging struts, oxygen-sensitive centers, and luminescent reporters. The newly developed probe featured excellent tolerance to harsh chemical environments, excellent photostability as well as pH-independent luminescence, rationalizing its suitability for DO sensing. Thanks to the homogeneous and well-isolated arrangement of the oxygen-accessible sites in the porous network, PCN-224(Pt) exhibited reversible phosphorescent response and excellent linear Stern–Volmer quenching behavior toward DO. A real-time analysis of DO during the process of enzyme-catalytic reaction exemplified its potentials in industrial and biological applications with oxygen involved.

# Highly Efficient NIR-II Photothermal Conversion Based on an Organic Conjugated Polymer\_2016

Copper nanoclusters (CuNCs) exhibit a high tendency to undergo oxidation particularly at the subnanometer size regime. In the light of overcoming this bottleneck, we have been successful in developing tripeptide (glutathione, GSH) templated CuNCs which show high biocompatibility and stability, in spite of being ultrafine in size. These blue-emitting CuNCs possess very promising optical features such as significant quantum yield (QY) and excellent photostability. Our cell-imaging studies reveal that the CuNCs localize primarily in nuclear membranes of the different cancerous (Hela, MDAMB-231, and A549) cells, and the cell viability assay conclusively established their nontoxic nature. Apart from their biological significances, these CuNCs also illustrate their ability to serve as a metal ion sensor, selectively detecting Fe3+ ions in solution at the nanomolar concentration regime. This unique luminescent property of the NCs will enable them to serve as label-free and versatile probes having several biological and analytical applications.

# Aggregation Control of Robust Water-Soluble Zinc(II) Phthalocyanine-Based Photosensitizers\_2016

The regioselective synthesis of fluorescent oligothiophene isothiocyanates is described. The isothiocyanates were reacted with bovine serum albumin (BSA) following standard procedures and the optical properties of the oligothiophene-BSA conjugates were analyzed as a function of oligomer concentration, time, and irradiation power. The oligothiophene-BSA conjugates were chemically very stable and their photoluminescence characteristics persisted unaltered for several months. Photoluminescence data relative to the conjugate of an oligothiophene-S,S-dioxide isothiocyanate with monoclonal anti-CD8 antibody are reported. No fluorescence quenching was observed following the binding of the isothiocyanate to the antibody and the conjugate displayed high chemical stability and photostability.

# Luminescent Copper Nanoclusters as a Specific Cell-Imaging Probe and a Selective Metal Ion Sensor\_2015

Photostability conditions as prescribed by ICH guidelines induced highly reduction-resistant scrambled disulfides that contribute to the population of apparent nonreducible aggregates in an IgG1 mAb. Photoinduced cross-linked species were isolated under reducing conditions using an organic phase size exclusion chromatography (OP-SEC) method, followed by O18-labeling tryptic mapping to identify cross-linked peptides. Disulfide scrambling was observed within the IgG1 structurally conserved-intrachain cysteine-cysteine-tryptophan triads (Cys-Cys-Trp), and correlated with Trp-to-kynurenine (Kyn) photodegradation within these triads. We hypothesize that intrachain disulfides protect the proximal Trp within the Cys-Cys-Trp triads from photodegradation by enabling dissipation of Trp-absorbed UV energy via electron transfer to the disulfide bond. Finally, we propose three distinct mechanisms of photochemical degradation of monoclonal antibodies mediated by Trp residues.

# Oligothiophene Isothiocyanates as a New Class of Fluorescent Markers for Biopolymers\_2001

We report here the use of a simple washing approach to reduce the ionic strength of the solution, which increased the thickness of the electric double layer on the surface of silver (Ag) nanoparticles and thereby enhanced their surface ζ-potential. This approach allowed us to prepare optically uniform (75−99%) and purified Ag nanoparticles (11.3 ± 2.3 nm) that are stable (nonaggregation) in solution for months, permitting them to become robust and widely used single nanoprobes for in vivo optical imaging. These Ag nanoparticles show remarkable photostability and serve as single nanoparticle photonic probes for continuous imaging nanoenvironments of segmentation-stage zebrafish embryos for hours. Unlike other particle tracking experiments, we utilized size-dependent localized surface plasmon resonance spectra (LSPRS) (colors) of single Ag nanoparticles to determine given colored (sized) nanoparticles in situ and used the monodisperse color (size) of nanoparticles to simultaneously measure viscosities and flow patterns of multiple proximal nanoenvironments in segmentation-stage zebrafish embryos in real time. We found new interesting counterclockwise flow patterns with rates ranging from 0.06 to 1.8 μm/s and stunningly high viscosity gradients spanning two orders of magnitude in chorion space of the embryos, with the highest viscosity observed around the center of chorion space and the lower viscosity at the interfacial areas near the surface of both chorion layers and inner mass of the embryos. This study demonstrates the possibility of using individual monodisperse nanophotonics to probe the roles of embryonic fluid dynamics in embryonic development.

# Photodisruption of the Structurally Conserved Cys-Cys-Trp Triads Leads to Reduction-Resistant Scrambled Intrachain Disulfides in an IgG1 Monoclonal Antibody\_2018

The conversion and degradation of organic pollutants remain challenges relating to environmental science. Herein, we report the carbonization of organic pollutants (4-nitrophenol, 4-NP) toward metal-free nitrogen-doped graphene quantum dots (N-GQDs) using a one-pot solvothermal route. The resultant N-GQDs demonstrate excellent activity for the catalytic conversion of 4-NP to 4-aminophenol (4-AP) when exposed to near-infrared (NIR) light because of their excellent upconverted photoluminescence and photothermal conversion ability. The NIR-enhanced reduction efficiency of 4-NP to 4-AP not only originates from the enhanced collisions between N-GQDs and 4-NP due to photothermal-increased Brownian movement of molecules but also comes from the accelerated transfer rate of electrons produced by the photoexcitation of N-GQDs under NIR irradiation. The N-GQDs display excellent photostability and remain with high activity even after five cycles of reuse. Such conversion of organic pollutants to highly efficient metal-free carbocatalysts has significant importance in the relevance of the industrial production of aniline and paracetamol.

# Design of Stable and Uniform Single Nanoparticle Photonics for In Vivo Dynamics Imaging of Nanoenvironments of Zebrafish Embryonic Fluids\_2008

Photothermal therapy (PTT) holds great promise for noninvasive cancer treatment. To fulfill this goal, highly effective and low-risk photothermal agents have been intensively explored. Here, we present a new PTT material based on conjugated polymer dots (Pdots) that exhibit strong near-infrared (NIR) absorption and high photostability. The Pdots result in a thermal response upon illumination with a NIR laser, leading to a high photothermal conversion efficiency of 65%. Thus, the photothermal ablation of cancer cells using the Pdots both in vitro and in vivo can be achieved, highlighting the potential of Pdots as a nanoplatform for clinical therapy. They also open up a new avenue to develop new photothermal therapeutic materials.

# Nitrogen-Doped Graphene Quantum Dots as Metal-Free Photocatalysts for Near-Infrared Enhanced Reduction of 4-Nitrophenol\_2019

We have synthesized dual-luminophore-doped silica nanoparticles for multiplexed signaling in bioanalysis. Two luminophores, Tris(2,2‘-bipyridyl)osmium(II)bis(hexafluorophosphate) (OsBpy) and Tris(2,2‘-bipyridyl)dichlororuthenium(II)hexahydrate (RuBpy), were simultaneously entrapped inside silica nanoparticles at precisely controlled ratios, with desirable sizes and required surface functionality. Single-wavelength excitation with dual emission endows the nanoparticles with optical encoding capability for rapid and high-throughput multiplexed detection. The nanoparticles can be prepared with sizes ranging from a few nanometers to a few hundred nanometers, with specific ratios of luminescence intensities at two well-resolved wavelengths and with excellent reproducibility. These nanoparticles also possess unique properties of high signal amplification, excellent photostability, and easy surface bioconjugation for highly sensitive measurements when used as signaling markers. A simplified ligand binding system using avidin−biotin and an application extension to immunoassays have been explored, demonstrating the potential use of these easily obtainable bioconjugated nanoparticles for multiplexed signaling and bioassays.

# Near-Infrared (NIR)-Absorbing Conjugated Polymer Dots as Highly Effective Photothermal Materials for In Vivo Cancer Therapy\_2016

Carbon monoxide (CO) is recognized as a biologically essential gaseous neurotransmitter that modulates many physiological processes in living subjects. Currently reported fluorescent probes for CO imaging in cells basically utilize palladium related chemistry which requires complicated synthetic work. Herein we provide a new strategy to construct a fluorescent nanoprobe, NanoCO-1, based on the Forster resonance energy transfer (FRET) mechanism by entrapping the existing dirhodium complex as the energy acceptor and the CO recognition part, and a commonly used nitrobenzoxadiazole (NBD) dye as energy donor into a micelle formed by self-assembly. The exchange of ligands in the dirhodium complex by CO in the nanoprobe disrupts the FRET and leads to the turn-on of fluorescence. The merits of NanoCO-1 including good biocompatibility, selectivity, photostability, and low cytotoxity, render this nanoprobe ability to track CO in living cells, zebrafish embryo, and larvae. Our straightforward approach can be extended to establish the CO fluorescent probes based on adsorption of CO on a variety of metal derivatives.

# Dual-Luminophore-Doped Silica Nanoparticles for Multiplexed Signaling\_2004

Here, we report a facile and green route to prepare Cu–In–S (CIS)/ZnS core/shell quantum dots (QDs) embedded in polyvinylpyrrolidone (PVP) solids and their application as phosphors for white light-emitting diodes (WLEDs). CIS/ZnS core–shell QDs were easily synthesized in the aqueous phase, assisted by microwave irradiation within 20 min at 95 °C. The emission wavelength of CIS/ZnS QDs could be tunable between a large range of 543–700 nm by adjusting the [Cu]/[In] ratios, and the photoluminescence (PL) quantum yield could be up to 43% by coating a ZnS layer. QD-embedded PVP solids then were facilely fabricated by mixing CIS/ZnS QDs and PVP in water, followed by drying, to show improved PL intensity, higher photostability, and higher thermostability. Finally, we demonstrated their potential application as a white light source by using green- and red-emitting CIS/ZnS/PVP nanocomposite solids as color converters, in combination with a blue light-emitting diode (LED) chip.

# Self-Assembled Fluorescent Nanoprobe Based on Forster Resonance Energy Transfer for Carbon Monoxide in Living Cells and Animals via Ligand Exchange\_2018

During the last 10 years, intense experimental and theoretical work has proven the existence of ultrafast nonradiative decay routes for UV-excited monomeric nucleic acid bases, accounting for their high photostability. This mechanism has been explained by the occurrence of easily accessible conical intersections connecting the first excited ππ\* state with the ground state. However, recent studies of substituent and solvent effects indicate that the situation is more complicated than what was initially thought, notably by the presence of dark excited states. Moreover, the actual shape of the excited-state potential energy surface may induce nonexponential dynamics. Further efforts are needed in order to clarify how various environmental factors affect the structural and dynamical aspects of the nucleic acid base excited states.

# Cu–In–S/ZnS Quantum Dots Embedded in Polyvinylpyrrolidone (PVP) Solids for White Light-Emitting Diodes (LEDs)\_2016

5-Methylcytosine (5mC) is the predominant epigenetic modification of DNA. 5mC and its sequential oxidation product, 5-hydroxymethylcytosine (5hmC), are crucial epigenetic markers which have a profound impact on gene stability, expression, and regulation. In the present work, ab initio electronic structure computations were performed to investigate the excited-state decay pathways for 5mC and 5hmC in both the neutral and protonated forms. Based on the theoretical quantities, four nonradiative decay pathways via conical intersections (CIs) were identified: ring distortion, ring opening, N–H dissociation, and intersystem crossing (ISC) pathways. Additional calculated potential energy surfaces revealed that ring distortion and ISC pathways were the most effective routes for 5mC and 5hmC, respectively. The influence of environmental factors, such as the solution and an acidic environment, was also explored in this study. Our study demonstrated that excited-state decay pathways via CIs are indispensable for the photostability of DNA epigenetic modifications and may be involved in ingenome stability and mammalian development.

# DNA/RNA: Building Blocks of Life Under UV Irradiation\_2010

Dual-functional probes, which not only enable visualization of diseased cells but also induce therapeutic cellular responses, are essential to biological studies. In the current work, a conjugated polyelectrolyte, PPET3-N2, was designed and synthesized as a dual-functional probe. The poly(phenylene ethynylene) terthiophene polymer backbone contributes to the polymer’s light-harvesting property to ensure the strong fluorescence as well as photosensitization, whereas quantanary ammonium side chains interact with target organelle for localization. As a fluorescent probe, PPET3-N2 was endocytosed to lysosomes through clathrin-mediated endocytosis (CME) and macropinocytosis (MPC) pathways. Colocalization of the probe with commercial fluorescent lysosome labels confirmed that this probe localized on lysosomes with high specificity and photostability. Real-time monitoring of autolysosome formation in autophagic cells was also demonstrated, providing a viable platform for cell-based screening of autophagy inhibitors. Finally, as a photosensitizer, PPET3-N2 can efficiently generate singlet oxygen in living cells upon irradiation of white light, leading to the destruction of lysosome membrane and release of ROS and lysosomal enzymes in cytoplasma, causing cell death.

# Computational Study on the Excited-State Decay of 5-Methylcytosine and 5-Hydroxymethylcytosine: The Common Form of DNA Methylation and Its Oxidation Product\_2018

We investigated the effects of annealing on the photoluminescence (PL) properties of a citrate-capped YVO4:Bi3+,Eu3+ nanophosphor. The 300 °C annealed nanophosphor exhibited the highest PL intensity at 619.5 nm corresponding to an f–f transition of Eu3+ under near-UV excitation. Fourier transform infrared spectroscopy indicated a decrease in the amounts of adsorbed water and citrate on the nanophosphor surface with annealing. Dehydration and the increase in near-UV absorption contributed to the improved PL intensity, since water is a Eu3+ luminescence quencher. The thermal decomposition of citrate, which photoreduces vanadate under near-UV irradiation, caused the improved photostability. Annealing at ≥400 °C decreased the PL intensity. A color change from white to yellow may be attributed to absorption by byproducts, possibly formed by the segregation of YVO4:Bi3+,Eu3+. A shorter PL lifetime and lower activation energy of thermal quenching at higher annealing temperature were confirmed from PL decay curves and the temperature dependence of PL intensity, respectively. The formation of surface defects resulted from the thermal decomposition of adsorbed citrate. The decrease in PL intensity was caused by the formation of byproducts and surface defects.

# Light-Induced Translocation of a Conjugated Polyelectrolyte in Cells: From Fluorescent Probe to Anticancer Agent\_2017

Shine a light on quantum dots, and depending on their exact size, the tiny semiconducting particles flicker a very specific color. This characteristic is what makes them attractive for use in display screens. But because of their small size and optical properties, quantum dots are increasingly being eyed for use in cell imaging, biomarker detection, and personal care products, according to Chemical Abstracts Service’s databases. Here, we highlight three emerging medical applications. Graphene Replaces Heavy Metals In Dots When scientists first attached green fluorescent protein (GFP) to a biomolecule of interest, they revolutionized the way proteins and other molecules are tracked in cells. But GFP’s fluorescence isn’t always stable, making long-term cell imaging difficult. Quantum dots, which are bright and have good photostability, are an alternative, but they have drawbacks too. Many quantum dots contain toxic heavy metals that might harm cells, and the dots themselves are often larger than ...

# Effects of Annealing on the Photoluminescence Properties of Citrate-Capped YVO4:Bi3+,Eu3+ Nanophosphor\_2014

A facile and efficient strategy to prepare multicolor and surface-functionalizable conjugated polymer nanoparticles (PPVseg-COOH CPNs) was demonstrated. The CPNs with tunable photoluminescence colors and carboxylate groups were further covalently modified with a series of specific molecules such as streptavidin, IgG and poly(ethylene glycol) to show their generality for subsequent bioconjugation and biological applications. The streptavidin coating can significantly improve the photostability of the PPVseg-SA CPNs, which indicates that specific biomolecules such as streptavidin functionalization of multicolor PPVseg-COOH CPNs can be applied to achieve high optical stability of CPNs in various buffer solutions, metal ions for many biological applications. Furthermore, the resulted PPVseg-SA CPNs also show efficient labeling ability in specific cellular imaging. The synthetic methods present the feasibility and versatility for further developing surface-functionalizable CPNs probes with full-color tunability for biological imaging and bioanalytical applications.

# Facile Preparation of Multicolor Polymer Nanoparticle Bioconjugates with Specific Biorecognition\_2014

Ab initio electronic-structure calculations indicate a mechanism for efficient excited-state deactivation of a low-energy conformer of the Gly-Phe-Ala tripeptide. The particularly short excited-state lifetime can explain the unexpected absence of this conformer in resonant two-photon ionization spectra. It is suggested that these ultrafast electronic deactivation processes provide specific conformers of peptides with a high degree of photostability.

# Patent Picks: Quantum Dots\_2015

Overall photocatalytic water splitting can proceed through a four-electron or two-electron/two-step pathway. However, it is challenging to manipulate the two- or four-electron pathway. Here, we present a carbon-based nanostructure codoped with nitrogen, sulfur, and a transition metal that exhibits reliable photocatalytic ability and satisfactory photostability in water splitting without the need for sacrificial agents. Note that in the present system the transition-metal-doped structure (M = Cr, Cd, Fe, Zn) as a photocatalyst splits water into H2 and O2 through a two-electron pathway while the structure on doping with rare-earth (Re) elements (M = Re = Sm, Ce, Eu, Pr, Er) acts as a photocatalyst via a four-electron pathway and carbon dots work herein as an electron acceptor and a reduction cocatalyst.

# Efficient Excited-State Deactivation of the Gly-Phe-Ala Tripeptide via an Electron-Driven Proton-Transfer Process\_2009

Silicon nanoparticles (Si NPs) have been widely used in fluorescence imaging. However, rigorous synthesis conditions and the single modality imaging limit the further development of Si NPs in the field of biomedical imaging. Here, we reported a method for synthesizing water-dispersible Mn2+ functionalized Si NPs (Mn–Si NPs) under mild experimental conditions for fluorescence and magnetic resonance dual-modality imaging. The whole synthesis process was completed under room temperature and atmospheric pressure, and no special and expensive equipment was required. The synthetic nanoparticles, with favorable pH stability, NaCl stability, photostability, and low toxicity, emitted green fluorescence (512 nm). At the same time, the nanoparticles also demonstrated excellent magnetic resonance imaging ability. In vitro, their T1-weighted magnetic resonance imaging effect was obvious, and the value of longitudinal relaxation degree r1 reached 4.25 mM–1 s–1. On the basis of their good biocompatibility, Mn–Si NPs were successfully used for the fluorescence imaging as well as magnetic resonance imaging in vivo.

# Control Strategy on Two-/Four-Electron Pathway of Water Splitting by Multidoped Carbon Based Catalysts\_2017

CdSe(core)/CdS(shell) nanorods (NRs) have been extensively investigated for their unique optical properties, such as high photoluminescence (PL) quantum efficiency (QE) and polarized light emission. The incorporation of these NRs in silica (SiO2) is of high interest, since this renders them processable in polar solvents while increasing their photochemical stability, which would be beneficial for their application in LEDs and as biolabels. We report the synthesis of highly luminescent silica-coated CdSe/CdS NRs, by using the reverse micelle method. The mechanism for the encapsulation of the NRs in silica is unravelled and shown to be strongly influenced by the NR shape and its asymmetry. This is attributed to both the different morphology and the different crystallographic nature of the facets terminating the opposite tips of the NRs. These results lead to the formation of a novel class of NR architectures, whose symmetry can be controlled by tuning the degree of coverage of the silica shell. Interestingly, the encapsulation of the NRs in silica leads to a remarkable increase in their photostability, while preserving their optical properties.

# Synthesis of Water-Dispersible Mn2+ Functionalized Silicon Nanoparticles under Room Temperature and Atmospheric Pressure for Fluorescence and Magnetic Resonance Dual-Modality Imaging\_2017

The present work explores the potential use of the conjugated cationic polyfluorene {[9,9-bis(6′-N,N,N-trimethylammonium)hexyl]fluorene-phenylene} bromide (HTMA-PFP) as a fluorescent membrane marker. To this end, the interaction of the polyelectrolyte with anionic model membranes has been investigated using different biophysical approaches. High affinity interaction was confirmed through alterations in the fluorescence spectrum of HTMA-PFP and by Förster resonance energy transfer (FRET) analysis. Quenching data indicate that once HTMA-PFP interacts with the membrane, it penetrates in the hydrophobic core embedded in the lipid bilayer where it presents high fluorescence quantum yield and photostability. Leakage experiments and dynamic light scattering (DLS) measurements show that the integrity of the lipid vesicles is maintained after polymer incorporation since no vesicle fusion or decomposition into small fragments is detectable. This conclusion is supported by fluorescence microscopy images, which confirm that polyelectrolyte interacts with the vesicle, labeling the lipid membrane without altering its morphology. Further experiments performed as a function of temperature indicate that the polymer is accommodated in the membrane without inducing significant loss of lipid cooperativity and without altering the packing of lipids within the bilayer. Finally, results show that polyelectrolyte fluorescence is sensitive to the large structural changes taking place in the lipid bilayer at the lipid phase transition. All these results confirm the ability of HTMA-PFP to visualize membrane structures and to monitor membrane processes.

# Synthesis of Highly Luminescent Silica-Coated CdSe/CdS Nanorods\_2013

Fluorescent peptide nanodots (PNDs) are bioorganic nanoparticles self-assembled from peptide biomolecules of different origin and complexity. These recently discovered nanodots of biological origin are highly promising for biomedical imaging applications due to their biocompatibility, bright and tunable fluorescence over the entire visible range and photostability. Here we apply single-particle microscopy methods to study the photophysical properties of individual PNDs. We show that the fluorescence spectrum tunability, studied previously only for PND ensembles in solutions, origins at the single-particle level. Temporal dynamics measurements of the single particles reveal fluorescence lifetime in the range of nanoseconds and pronounced fluorescence blinking with continuous bright states of seconds. The latter provides a first evidence of quantum emitter transitions between two states (ON and OFF) in fluorescent PNDs. All these findings advance the understanding of the fluorescence mechanism of PNDs and provide strong motivation for using PNDs as fluorescent agents for various bioimaging and super-resolution techniques.

# Use of the Conjugated Polyelectrolyte Poly{[9,9-bis(6′-N,N,N-trimethylammonium)hexyl]fluorene-phenylene} Bromide (HTMA-PFP) as a Fluorescent Membrane Marker\_2013

A multifunctional architecture for biomedical applications has been developed by deliberately combining the useful functions of superparamagnetism, luminescence, and surface functionality into one material. Good control of the core−shell architecture has been achieved by employing a sol−gel synthesis. Superparamagnetic iron oxide nanoparticles are first coated with silica to isolate the magnetic core from the surrounding. Subsequently, the dye molecules are doped inside a second silica shell to improve photostability and allow for versatile surface functionalities. The architecture has been characterized by transmission electron microscopy, UV−vis absorption and emission spectroscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and magnetometry. The hybrid nanoparticles exhibit improved superparamagnetic behavior over the as-received nanoparticles with a significant decrease in the blocking temperature. The architecture shows emission properties similar to those of the free dye molecules, suggesting that the first silica shell successfully prevents luminescence quenching by minimizing dye−magnetic core interactions.

# Single Fluorescent Peptide Nanodots\_2019

Fluorescent films were fabricated by depositing Y2O3:Bi3+,Eu3+ nanosheets, which emit red light under near-UV irradiation. The Y2O3:Bi3+,Eu3+ nanosheets were obtained by calcining hydroxide precursor nanosheets synthesized through a hydrothermal method. An aqueous dispersion of positively charged Y2O3:Bi3+,Eu3+ nanosheets with polyethyleneimine adsorbed to the surface was prepared for their deposition. Fluorescent nanosheets were electrophoretically deposited on a transparent conductive substrate under a constant voltage. The obtained nanosheet films were dense and uniform and showed excellent photostability against the excitation light. Growth of the nanosheet film caused a decrease in transmittance and an increase in the photoluminescence intensity. The former effect was attributed to light scattering from inner voids and the rough surface of the film. A polyvinylpyrrolidone (PVP) coating on the film improved the transmittance to be greater than 70% over the visible region. These effects were attributed to antireflection effects at the film surface owing to the low refractive index of PVP. Furthermore, suppression of light scattering by coating the rough surface with a smooth PVP film and filling of voids in the nanosheet film with PVP also improved the transmittance.

# Multifunctional Nano-Architecture for Biomedical Applications\_2006

Lignin nanospheres with broad-spectrum UV adsorption and excellent antioxidant properties were obtained by demethoxylation of alkali lignin (AL) and grafting the benzophenone moiety (UV-0) followed by a reverse self-assembly. The critical wavelength (λc) of the optimal AL-UV03 sample was ∼375 nm, while the UVA/UVB ratio reached 0.84. When it was applied as a unique active in sun cream, the sun protection factor value of the cream containing 10 wt % AL-UV03 was 22.81, which could further increase to 56.14 when it formed reverse colloidal spheres (LRCS) with a size of ∼130 nm. The self-assembly process and the UV-absorbing enhancement mechanism of LRCS were monitored and revealed by fluorescence, UV, and light scattering analysis. In addition, AL-UV03 exhibited superior photostability due to the three-dimensional network structure of lignin. The antioxidant activities of AL-UV03 and LRCS were better than that of AL and could increase continuously with the dosage. Both AL-UV03 and LRCS exhibited good biocompatibility. HaCaT cell activity remained 72–78% when their concentration was as high as 1.0 mg/mL. The novel lignin broad-spectrum UV blocker and antioxidant show good potential in skincare products and polymeric materials.

# Electrophoretically Deposited Y2O3:Bi3+,Eu3+ Nanosheet Films with High Transparency for Near-Ultraviolet to Red Light Conversion\_2018

Easy preparation, high stability, prominent activity, and excellent recyclability are four key elements for high-performance heterogeneous photocatalysts. Developing covalent organic framework (COF)-based heterogeneous photocatalysts possessing all of these traits is highly challenging. In this study, we successfully synthesized an imine-linked BBO-COF by the “two-in-one” strategy featuring the above four merits. Highly crystalline and porous BBO-COF can be easily prepared in at least 11 different simplex solvents independent of their polarity and boiling points and even under an air atmosphere. Moreover, BBO-COF exhibits extraordinary chemical stability and photostability in strong acid (12 M HCl), corrosive base (12 M NaOH), and visible light for 7 days. Furthermore, BBO-COF exhibited prominent photocatalytic activity toward oxidative hydroxylation reaction of arylboronic acids with excellent substrates tolerance and reusability. This “two-in-one” design strategy open a new avenue for facile constructing novel functional COFs with tailor-made properties.

# Enhancing the Broad-Spectrum Adsorption of Lignin through Methoxyl Activation, Grafting Modification, and Reverse Self-Assembly\_2019

The electronic properties of colloidal quantum dots (CQDs) have shown intriguing potential in recent years for implementation in various optoelectronic applications. However, their chemical and photochemical stabilities, mainly derived from surface properties, have remained a major concern. This paper reports a new strategic route for the synthesis of surface-treated CQDs, the CdSe/CdS core/shell heterostructures, based on low-temperature coating of a shell constituent, followed by a programmed annealing process. A comprehensive follow-up of the stability and the optical properties through the various synthesis stages is reported, suggesting that the low-temperature coating is responsible for the formation of a sharp interface between the core and the shell, whereas a postcoating annealing process leads to the generation of a thin alloy interfacial layer. At the end of the process, the CdSe/CdS CQDs show a significant improvement of the photoluminescence quantum yield, as well as an exceptional photostability. Consequently, the work reported here provides a convenient generic route to the formation of core/shell CQDs to be employed as a procedure for achieving various other heterostructures.

# Ultrastable Covalent Organic Frameworks via Self-Polycondensation of an A2B2 Monomer for Heterogeneous Photocatalysis\_2019

Photoreactivity can be influenced by mechanical forces acting over a reacting chromophore. Nevertheless, the specific effect of the external forces in the photoreaction mechanism remains essentially unknown. Conical intersections are key structures in photochemistry, as they constitute the funnels connecting excited and ground states. These crossing points are well known to provide valuable information on molecular photoreactivity, including crucial aspects as potential photoproducts which may be predicted by just inspection of the branching plane vectors. Here, we outline a general framework for understanding the effect of mechanical forces on conical intersections and their implications on photoreactivity. Benzene S1/S0 conical intersection topology can be dramatically altered by applying less than 1 nN force, making the peaked pattern of the intersection become a sloped one, also provoking the transition state in the excited state to disappear. Both effects can be related to an increase in the photostability as the conical intersection becomes more accessible, and its topology in this case favors the recovery of the initial reactant. The results indicate that the presence of external forces acting over a chromophore have to be considered as a potential method for photochemical reactivity control.

# Comprehensive Route to the Formation of Alloy Interface in Core/Shell Colloidal Quantum Dots\_2015

Photothermal therapy (PTT) is attracting increasing interest and becoming more widely used for skin cancer therapy in the clinic, as a result of its noninvasiveness and low systemic adverse effects. However, there is an urgent need to develop biocompatible PTT agents, which enable accurate imaging, monitoring, and diagnosis. Herein, a biocompatible Gd-integrated CuS nanotheranostic agent (Gd:CuS@BSA) was synthesized via a facile and environmentally friendly biomimetic strategy, using bovine serum albumin (BSA) as a biotemplate at physiological temperature. The as-prepared Gd:CuS@BSA nanoparticles (NPs) with ultrasmall sizes (ca. 9 nm) exhibited high photothermal conversion efficiency and good photostability under near-infrared (NIR) laser irradiation. With doped Gd species and strong tunable NIR absorbance, Gd:CuS@BSA NPs demonstrate prominent tumor-contrasted imaging performance both on the photoacoustic and magnetic resonance imaging modalities. The subsequent Gd:CuS@BSA-mediated PTT result shows high therapy efficacy as a result of their potent NIR absorption and high photothermal conversion efficiency. The immune response triggered by Gd:CuS@BSA-mediated PTT is preliminarily explored. In addition, toxicity studies in vitro and in vivo verify that Gd:CuS@BSA NPs qualify as biocompatible agents. A biodistribution study demonstrated that the NPs can undergo hepatic clearance from the body. This study highlights the practicality and versatility of albumin-mediated biomimetic mineralization of a nanotheranostic agent and also suggests that bioinspired Gd:CuS@BSA NPs possess promising imaging guidance and effective tumor ablation properties, with high spatial resolution and deep tissue penetration.

# Mechanical Forces Alter Conical Intersections Topology\_2015

The highly emissive nanoparticles Gn-TCMPE (n = 0–4) were prepared by using PAMAM dendrimers as “molecular glue” to adhere an AIE-active molecule tetra(4-(carboxymethoxy)phenyl)ethylene (TCMPE). The electrostatic interaction of ammonium–carboxylate ion pairs provides a driving force between TCMPE and PAMAM dendrimers to form the nanoparticles Gn-TCMPE (n = 0–4), which is validated by the FTIR and 1H NMR spectra. The formation of nanoparticles dramatically blocks the nonradiative pathway and enhances the fluorescence of TCMPE. The quantum yields of Gn-TCMPE gradually boost at first and then reach to a plateau with increasing the generation of PAMAM dendrimers, and the highest absolute quantum yields are obtained to be 0.42 and 0.64 for Gn-TCMPE (n = 2–4) in methanol dispersion and solid phases, respectively. The fluorescence of the nanoparticles can be tuned by addition of trifluoroacetic acid (TFA). Furthermore, the G4-TCMPE has been successfully applied to selectively image cytoplasm of Hela cells with excellent photostability and low cytotoxicity. This study provides a novel noncovalent strategy for developing highly emissive and robust organic materials fitting for cell fluorescence imaging.

# Albumin-Bioinspired Gd:CuS Nanotheranostic Agent for In Vivo Photoacoustic/Magnetic Resonance Imaging-Guided Tumor-Targeted Photothermal Therapy\_2016

Fluorescence (FL)/magnetic resonance (MR) dual-modal imaging nanoprobes are significant not only for cutting edge research in molecular imaging, but also for clinical diagnosis with high precision and accuracy. However, synthesis of FL/MR dual-modal imaging nanoprobes that simultaneously exhibit strong fluorescent brightness and high MR response, long-term colloidal stability with uniform sizes, good biocompatibility and a versatile surface functionality has proven challenging. In this study, the well-defined core–shell structured Gd3+ chelate-conjugated fluorescent polymer nanoparticles (Gd-FPNPs) that consist of rhodamine B (RB)-encapsulated poly(methyl methacrylate) (PMMA) cores and Gd3+ chelate-conjugated branched polyethylenimine (PEI) shells, are facilely synthesized via a one-step graft copolymerization of RB-encapsulated MMA from PEI-DTPA-Gd induced by tert-butyl hydroperoxide (TBHP) at 80 °C for 2 h. The mild synthesis route not only preserves the chemical environment for Gd3+ coordination, but also improves optical properties and chemo-/photostability of RB. A high local concentration of outer surface-chelated Gd3+ and their direct interactions with hydrogen protons endow Gd-FPNPs high longitudinal relaxivity (26.86 mM–1 s–1). The uniform spherical structure of Gd-FPNPs facilitates their biotransfer, and their surface carboxyl and amine groups afford them both long-term colloidal stability and cell-membrane permeability. The excellent biocompatibility and FL/MR dual-modal imaging capability of Gd-FPNPs are demonstrated using HeLa cells and mice as models. All the results confirm that Gd-FPNPs fulfill the design criteria for a high-performance imaging nanoprobe. In addition, this study enables such probes to be prepared also by those not skilled in nanomaterial synthesis, and thus promoting the development of novel functional imaging nanoprobes.

# Highly Emissive Nanoparticles Based on AIE-Active Molecule and PAMAM Dendritic “Molecular Glue”\_2015

A water-soluble fluorescent hyperbranched conjugated polyelectrolyte (HCPE) with a unique double-layered architecture is synthesized via the combination of alkyne polycyclotrimerization and alkyne-azide “click” reaction for live-cell imaging. Because of the rigid conjugated core that offers shape persistence, and the water-soluble nonionic poly(ethylene glycol) shells that passivate the macromolecular surface, HCPE intrinsically forms single-molecular core−shell nanospheres with an average diameter of ∼10.7 nm and a narrow size distribution of ∼1.5, according to transmission electron microscopy images. The resulted organic nanospheres possess high quantum yield (30% in buffer), good solution stability, and low cytotoxicity. Using breast cancer cell MCF-7 as an example, these core−shell nanospheres are internalized efficiently by the cells and accumulated in the cytoplasm to give bright fluorescence. Photostability study reveals that these nanospheres are significantly more stable than commercial dyes, such as fluorescein, rhodamine, and Cy5, which demonstrates the great potential of organic polymeric nanomaterials in long-term clinical applications. In addition, the state-of-the-art synthetic methods used herein provide the feasibility and flexibility to modify both core and shell components of HCPE for specific biological applications.

# Facile Synthesis of Gadolinium Chelate-Conjugated Polymer Nanoparticles for Fluorescence/Magnetic Resonance Dual-Modal Imaging\_2018

We synthesized tiny stable silver nanoparticles (2.6 ± 1.1 nm) and used its small surface area and functional groups to control single molecule detection (SMD) volumes on single nanoparticles. These new approaches allowed us to develop intrinsic single molecule nanoparticle optical biosensors (SMNOBS) for sensing and imaging of single human cytokine molecules, recombinant human tumor necrosis factor-α (TNFα), and probing its binding reaction with single monoclonal antibody (MAB) molecules in real-time. We found that SMNOBS retained their biological activity over months and showed exceptionally high photostability. Our study illustrated that smaller nanoparticles exhibited higher dependence of optical properties on surface functional groups, making it a much more sensitive biosensor. Localized surface plasmon resonance spectra (LSPRS) of SMNOBS showed a large red shift of peak wavelength of 29 ± 11 nm, as single TNFα molecules bound with single MAB molecules on single nanoparticles. Utilizing its LSPRS, we quantitatively measured its binding reaction in real time at single molecule (SM) level, showing stochastic binding kinetics of SM reactions with binding equilibrium times ranging from 30 to 120 min. SMNOBS exhibited extraordinarily high sensitivity and selectivity, and a notably wide dynamic range of 0−200 ng/mL (0−11.4 nM). Thus, SMNOBS is well suited for the fundamental study of biological functions of single protein molecules and SM interactions of chemical functional groups with the surface of nanoparticles, as well as development of effective disease diagnosis and therapy.

# Fluorescent Single-Molecular Core−Shell Nanospheres of Hyperbranched Conjugated Polyelectrolyte for Live-Cell Imaging\_2009

As a rising star in the family of fluorescent material, graphene quantum dots (GQDs) have attracted great attention because of their excellent properties such as high photostability against photobleaching and blinking, biocompatibility, and low toxicity. Herein, blue luminescent GQDs were prepared by photo–reducing GQDs with isopropanol. After photochemical reduction, the increasing of sp2 domains and the formed hydroxyl in pGQDs can enhance the photoluminescence of GQDs. The quantum yield of the photo–reduced GQDs (pGQDs) was increased 3.7 fold. Because of its less negative surface charges and lower cytotoxicity than chemical reduced GQDs (cGQDs), the pGQDs were more easily uptaken by cells. This work may provide a simple and green pathway to enhance the QY of GQDs with satisfactory biocompatibility as fluorescent nanoprobes.

# Photostable Single-Molecule Nanoparticle Optical Biosensors for Real-Time Sensing of Single Cytokine Molecules and Their Binding Reactions\_2008

While perovskite nanocrystals (NCs) have shown great promise as materials for efficient light-emitting diodes (LEDs), low photoluminescence quantum yield (PLQY) of the blue-emitting perovskites is an impediment to the development of white LEDs of which blue is an essential component. Herein, we report that room temperature postsynthetic treatment of weakly blue-violet-emitting (PLQY 3%) CsPbCl3 NCs with CdCl2 results in an instantaneous enhancement of the PLQY to near-unity without affecting the PL peak position (406 nm) and spectral width. The time-resolved PL and ultrafast transient absorption measurements confirm the removal of nonradiative defect states of the CsPbCl3 NCs in treated sample. The elemental composition and structural data of the treated sample reveal facile doping of Cd2+ into the crystal lattice without affecting the size and shape of the NCs. Extraordinary PLQY, high air stability and photostability and ease of preparation of this Cd-doped CsPbCl3 make it by far the most attractive blue-emitting perovskite for development of efficient blue and white LEDs.

# Improvement of Photoluminescence of Graphene Quantum Dots with a Biocompatible Photochemical Reduction Pathway and Its Bioimaging Application\_2013

Photobleaching of fluorophores is one of the key problems in fluorescence microscopy. Overcoming the limitation of the maximum number of photons, which can be detected from a single emitter, would allow one to enhance the signal-to-noise ratio and thus the temporal and spatial resolution in fluorescence imaging. It would be a breakthrough for many applications of fluorescence spectroscopy, which are unachievable up to now. So far, the only approach for diminishing the effect of photobleaching has been to enhance the photostability of an emitter. Here, we present a fundamentally new solution for increasing the number of photons emitted by a fluorophore. We show that, by exposing a single SiO2 nanoparticle to UV illumination, one can create new luminescent centers within this particle. By analogy with nanodiamonds, SiO2 nanoparticles can possess luminescent defects in their regular SiO2 structure. However, due to the much weaker chemical bonds, it is possible to generate new defects in SiO2 nanostructures using UV light. This allows for the reactivation of the nanoparticle’s fluorescence after its photobleaching.

# Achieving Near-Unity Photoluminescence Efficiency for Blue-Violet-Emitting Perovskite Nanocrystals\_2018

Developing probes for the detection of reactive oxygen species (ROS), a hallmark of many pathophysiological process, is imperative to both understanding the precise roles of ROS in many life-threatening diseases and optimizing therapeutic interventions. We herein report an all-in-one fluorescent semiconducting polymer based far-red to near-infrared (NIR) Pdot nanoprobe for the ratiometric detection of hypochlorous acid (HOCl). The fabrication takes the advantage of flexible polymer design by incorporating target-sensitive and target-inert fluorophores into a single conjugated polymer to avoid leakage or differential photobleaching problems existed in other nanoprobes. The obtained nanoprobe has improved performance in HOCl sensing, such as high brightness, ideal far-red to NIR optical window, excellent photostability, self-referenced ratiometric response, fast response, and high selectivity. The dual-emission property allows the sensitive imaging of HOCl fluctuations produced in living macrophage cells and peritonitis of living mice with high contrast. This study not only provides a powerful and promising nanoprobe to be potentially used in the investigations of in situ HOCl status of diseases in living systems but also puts forward the design strategy of a new category of ratiometric fluorescent probes facilitating precise and reliable measurement in biological systems.

# Photoactivation of Luminescent Centers in Single SiO2 Nanoparticles\_2016

The construction of safe and stable theranostics is beneficial to realize simultaneous cancer diagnosis and treatment. In this study, bovine serum albumin–gadolinium (BSA–Gd) complexes and MoS2 nanoflakes (MoS2–Gd–BSA) were successfully married as cancer theranostics for dual-modality magnetic resonance (MR)/photoacoustic (PA) imaging and photothermal therapy (PTT). BSA–Gd complexes were prepared by the biomineralization method and then conjugated with MoS2 nanoflakes via an amide bond. The as-prepared MoS2–Gd–BSA possessed a good photostability and photothermal effect. The cytotoxicity assessment and hemolysis assay suggested the excellent biocompatibility of MoS2–Gd–BSA. Meanwhile, MoS2–Gd–BSA could not only achieve in vivo MR/PA dual-modality imaging of xenograft tumors, but also effectively kill cancer cells in vitro and ablate the xenograft tumors in vivo upon 808 nm laser illumination. The biodistribution and histological evaluations indicated the negligible toxicity of MoS2–Gd–BSA both in vitro and in vivo. Thus, our results substantiated the potential of MoS2–Gd–BSA for cancer theranostics.

# Photostable Ratiometric Pdot Probe for in Vitro and in Vivo Imaging of Hypochlorous Acid\_2017

Cyclometalated iridium(III) coumarin complexes represent new types of probes for optical oxygen sensing. In comparison to the most commonly used ruthenium(II) polypyridyl dyes and porphyrin complexes with platinum group metals, they possess much more efficient visible absorption and higher quantum yields, which results in much higher brightnesses. Spectral properties and oxygen sensitivity can be fine-tuned by varying the nature of the coumarin ligand and using respective monomeric or dimeric complexes. When incorporated in a model polystyrene film the probes show optimal dynamics of luminescence decay time for oxygen monitoring in the range from 0% to 100% air saturation. Cross-sensitivity to temperature is significantly lower than for the commonly used ruthenium(II)-tris-4,7-diphenyl-1,10-phenanthroline oxygen probe. The probes, however, exhibit significantly lower photostability, which restricts their application. If long-term measurements are not required, the probes can be successfully used for reliable monitoring of oxygen concentration. High brightness of the complexes makes them particularly attractive for application in thin films (for monitoring of fast processes) and various types of nano- and microparticles, including magnetic beads. If temperature compensation is not applied, the novel optodes result in the lower errors in determination of oxygen content.

# Marriage of Albumin–Gadolinium Complexes and MoS2 Nanoflakes as Cancer Theranostics for Dual-Modality Magnetic Resonance/Photoacoustic Imaging and Photothermal Therapy\_2017

In clinical studies, thiol measurement in the whole blood is of diagnostic and prognostic significance. In addition, the detection of mitochondrial thiol is very important for investigating cellular functions or dysfunctions. Here, a ratiometric aggregation-induced emission luminogen (AIEgen) called TPE-PBP for thiol detection was developed by introducing a para-dinitrophenoxy benzylpyridinium moiety to tetraphenylethylene. TPE-PBP exhibits excellent biocompatibility, high photostability, and large two-photon absorption cross-section. TPE-PBP emits red fluorescence in PBS buffer without thiol. Upon addition of thiol, there is a gradual blue shift of TPE-PBP’s emission with ratiometric fluorescent response because of cleavage of the dinitrophenyl ether bond by thiol followed by the self-immolation of the para-hydroxybenzyl moiety to produce a less conjugated AIEgen. The in vitro quantification of thiol is enabled by the linear ratiometric fluorescence response with a very low limit of detection. Considering the high sensitivity and good selectivity toward thiol detection, TPE-PBP was also utilized to detect thiol in the blood. Furthermore, mitochondrial thiols in vitro, ex vivo, and in vivo were quantitatively mapped by TPE-PBP using fluorescence microscopy under one- and two-photon conditions.

# Ultrabright Oxygen Optodes Based on Cyclometalated Iridium(III) Coumarin Complexes\_2007

Adenosine triphosphate (ATP) is used as the energy source in cells and plays crucial roles in various cellular events. The cellular membrane is the protective barrier for the cytoplasm of living cells and involved in many essential biological processes. Many fluorescent probes for ATP have been successfully developed, but few of these probes were appropriate for visualizing ATP level fluctuation in cell membranes during the apoptotic cell death process. Herein, we report the synthesis of a new water-soluble cationic polythiophene derivative that can be utilized as a fluorescent sensor for detecting ATP in cell membranes. Poly((3-((4-methylthiophen-3-yl)oxy)propyl)triphenylphosphonium chloride) (PMTPP) exhibits high sensitivity and good selectivity to ATP, and the detection limit is 27 nM. The polymer shows low toxicity to live cells and excellent photostability in cell membranes. PMTPP was practically utilized for real-time monitoring of ATP levels in the cell membrane through fluorescence microscopy. We have demonstrated that the ATP levels in cell membranes increased during the apoptotic cell death process. The probe was also capable of imaging ATP levels in living mice.

# Ratiometric Detection of Mitochondrial Thiol with a Two-Photon Active AIEgen\_2019

Nitrogen-doped (N-doped) photoluminescent carbon dots (CDs) were prepared by a one-pot microwave-assisted hydrothermal treatment using histidine as the sole carbon source in the absence of acid, alkali, or metal ions. With a diameter of 2–5 nm, the synthesized CDs had apparent lattice fringes and exhibited an excitation-dependent photoluminescent behavior. The CDs were highly yielded, well-dispersed in aqueous solution, and showed high photostability in the solutions of a wide range of pH and salinity. They were used as probes to identify the presence of Fe3+ ions with a detection limit of 10 nM. With confirmed nontoxicity, these CDs could enter the cancer cells, indicating a practical potential for cellular imaging and labeling.

# Water-Soluble Conjugated Polymer as a Fluorescent Probe for Monitoring Adenosine Triphosphate Level Fluctuation in Cell Membranes during Cell Apoptosis and in Vivo\_2017

2-(2‘-Hydroxy-5‘-methylphenyl)benzotriazole, 1, Tinuvin P, and o-hydroxybenzophenone, 2, are thought to achieve exceptional photostability through highly reversible deactivation associated with their intramolecular hydrogen bonds. Excimer laser excitation (10 mJ, 20 ns at 308 nm) of these molecules in argon-bubbled hexane solution at room temperature affords no discernible transient signals (absorption or emission) between 320 and 800 nm. In DMSO solution under the same conditions, however, strong transient absorptions in the visible (λmax 410 and 425 nm for 1 and 2, respectively) are observed. The transients responsible for the absorptions are quenched by oxygen and acid, and the spectra match well with the ground state difference spectra generated from the corresponding phenolate ions. When a bulky group is incorporated ortho to the hydroxyl function such as in 2-(2‘-hydroxy-3‘-cumyl-5‘-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 3, Tinuvin 928, no appreciable transient absorption is observed even in DMSO solution. These results are consistent with the disruption of the intramolecular hydrogen bond of 1 and 2 (but not 3) as the result of intermolecular hydrogen bond formation with DMSO. The “dramatic” ortho effect implies that the bulky group adjacent to the hydroxyl function sterically shields the intramolecular hydrogen bond from disruption by polar basic environments.

# Histidine-Derived Nontoxic Nitrogen-Doped Carbon Dots for Sensing and Bioimaging Applications\_2014

O-Hydroxybenzaldehyde (OHBA) is a prototypical photoprotector exhibiting excited-state intramolecular proton transfer (ESIPT). Here we report how its photostability depends on an extended conical intersection seam associated with a manifold of decay paths. Thus, the photoreactivity of OHBA derives from a flat excited-state potential energy surface with barriers of only tenths of electronvolts between the reactant and several conical intersection structures that lead to different products: two isomers of a hydrogen-bonded intersection (HBI) that lead back to the enol reactant or to the tautomerized keto form in its Z conformation; an intersection (ZEI) that mediates the Z-E isomerization of the keto tautomer; and a twisted-pyramidalized one (TPI) that leads to an oxetene adduct. The intersection structures are connected to each other, forming a continuous seam, and the competition between the products depends on where the seam is accessed after the initial excitation. The overall picture must be also valid for the methyl salicylate and salicylic acid analogues of OHBA since it reflects the characteristics reported previously for MS and SA.

# DMSO Solvent Induced Photochemistry in Highly Photostable Compounds. The Role of Intermolecular Hydrogen Bonding\_1997

There has been growing interest in utilizing highly photostable iridium(III) complexes as new luminescent probes for biotechnology and life science. Herein, iridium(III) complex with carboxyl group was synthesized and activated with N-hydroxysuccinimide, followed by tagging to the amino terminate of single-stranded DNA (ssDNA). The Ir-ssDNA probe was further combined with graphene oxide (GO) nanosheets to develop a GO-based biosensor for target ssDNA detection. The quenching efficiency of GO, and the photostability of iridium(III) complex and GO-Ir-ssDNA biosensor, were also investigated. On the basis of the high luminescence quenching efficiency of GO toward iridium(III) complex, the GO-Ir-ssDNA biosensor exhibited minimal background signals, while strong emission was observed when Ir-ssDNA desorbed from GO nanosheets and formed a double helix with the specific target, leading to a high signal-to-background ratio. Moreover, it was found that luminescent intensities of iridium(III) complex and GO-Ir-ssDNA biosensor were around 15 and 3 times higher than those of the traditional carboxyl fluorescein (FAM) dye and the GO-FAM-ssDNA biosensor after UV irradiation, respectively. Our study suggested the sensitive and selective Ir-ssDNA probe was suitable for the development of highly photostable GO-based detection platforms, showing promise for application beyond the OLED (organic light emitting diode) area.

# An Extended Conical Intersection Seam Associated with a Manifold of Decay Paths: Excited-State Intramolecular Proton Transfer in O-Hydroxybenzaldehyde\_2008

MoS2 crystals exhibit excellent catalytic properties and great potential for photocatalytic production of solar fuels such as hydrogen gas. In this regard, the photocatalytic stability of exfoliated single- and few-layer MoS2 immersed in water is investigated by μ-Raman spectroscopy. We find that while the basal plane of MoS2 can be treated as stable under photocatalytic conditions, the edge sites and presumably also defect sites are highly affected by a photoinduced corrosion process. The edge sites of MoS2 monolayers are significantly more resistant to photocatalytic degradation compared to MoS2 multilayer edge sites. The photostability of MoS2 edge sites depends on the photon energy with respect to the band gap in MoS2 and also on the presence of oxygen in the electrolyte. These findings are interpreted in the framework of an oxidation process converting MoS2 into MoOx in the presence of oxygen and photoinduced charge carriers. The high stability of the MoS2 basal plane under photocatalytic treatment under visible light irradiation of extreme light intensities on the order of P ≈ 10 mW/μm2 substantiates MoS2’s potential as photocatalyst for solar hydrogen production.

# Luminescent Iridium(III) Complex Labeled DNA for Graphene Oxide-Based Biosensors\_2016

Gold nanorods (GNRs) were initially prepared with three different aspect ratios (2.5, 2.9, and 3.8) via a seed-mediated chemical route, using cetyltrimethylammonium bromide (CTAB) as the organic surfactant. These rods were then irradiated under continuous-wave (λ = 1064 nm) and pulsed (λ = 1064, 532, 355 nm) emission modes using Nd:YVO4 and Nd:YAG lasers, respectively. The photostability and behavior of the Au nanorods under these laser irradiation conditions were studied using UV–vis–nIR spectroscopy and electron microscopy. Photofragmentation and melting mechanisms were provoked as a function of laser irradiation parameters (emission mode and wavelength) and caused the GNRs to undergo considerable morphological changes. Important differences were observed between the wavelengths used for irradiation, indicating significantly different nanorod breakdown mechanisms.

# Photocatalytic Stability of Single- and Few-Layer MoS2\_2015

We report observations of a dark state in the decay pathways of thymine, 1,3-dimethyl thymine, 1,3-dimethyl uracil, and 1-methyl uracil in the gas phase. After initial excitation by a nanosecond laser, the excited molecules failed to return to the ground state but rather were trapped in a dark state for tens to hundreds of nanoseconds. This result contradicts those reported in water solutions. We therefore propose that the photochemistry of these pyrimidine bases is different in the gas phase from that in the liquid phase and that the dark state is effectively quenched in water solutions. Although we do not have a quantitative measure of the yield of this dark state, the fact that further ionization from this dark state has a high yield in the deep UV makes this pathway important in the chemistry of nucleic acid bases. This result further implies that the photostability of our genetic code may not be an inherent property of the bases themselves.

# Transformation of Gold Nanorods in Liquid Media Induced by nIR, Visible, and UV Laser Irradiation\_2015

We have prepared supramolecular assemblies of hexaaryl-anchored polyester zinc(II) porphyrin dendrimers (6PZnW, 12PZnW, and 24PZnW) with various bipyridyl guests (CnPy2; n = 1, 2, 4, 6, and 8) through self-assembled coordination to control the structures and photophysical properties. We comparatively investigated the photophysical properties of porphyrin dendrimers with and without guest binding by using ensemble and single-molecule spectroscopy. The spectrophotometric titration data of dendrimers with guest molecules provide a strong indication of the selective intercalation of bipyridyl guests into porphyrin dendrimers. The representative dendrimer assembly 12PZnW⊃C6Py2 exhibits increased fluorescence quantum yield and lifetime in ensemble measurements, as well as higher initial photon count rates with stepwise photobleaching behavior in the single-molecule fluorescence intensity trajectories (FITs) compared to 12PZnW. At the single-molecule level, the higher photostability of 12PZnW⊃C6Py2 can be deduced from the long durations of the first emissive levels in the FITs. We attribute the change in photophysical properties of the dendrimer assemblies to their structural changes upon intercalation of guest molecules between porphyrin units. These results provide new insight into the control of porphyrin dendritic structures using appropriate bidentate guests in poor environmental conditions.

# Decay Pathways of Thymine and Methyl-Substituted Uracil and Thymine in the Gas Phase\_2003

Photothermal conversion in the second near-infrared (NIR-II) window allows deeper penetration and higher exposure to lasers, but examples of NIR-II photothermal agents are mainly formulated by inorganic compounds. In view of the underlying influence of inorganic materials, a novel NIR-II photothermal nanoagent based on a narrow band gap D–A conjugated polymer (TBDOPV–DT) with 2,2-bithiophene as the donor and thiophene-fused benzodifurandione-based oligo(p-phenylenevinylene) as the acceptor has been developed. More importantly, TBDOPV–DT nanoparticles (TBDOPV–DT NPs) are demonstrated to combine excellent photoacoustic imaging (PAI) and photothermal therapy (PTT) ability. TBDOPV–DT NPs exhibit dramatic photostability and heating reproducibility with a photothermal conversion efficiency of 50%. Especially, the NPs possess a remarkable PTT effect toward cancer cells in vitro and can eliminate tumor cells completely in vivo under 1064 nm laser irradiation, while no appreciable side effects have been observed. This study achieves PAI-guided cancer therapy and sheds light on the future of using organic polymer NPs for the NIR-II PTT of cancer.

# Control of Molecular Structures and Photophysical Properties of Zinc(II) Porphyrin Dendrimers Using Bidentate Guests: Utilization of Flexible Dendrimer Structures as a Controllable Mold\_2008

A continuing goal of nanoparticle (NP)-mediated drug delivery (NMDD) is the simultaneous improvement of drug efficacy coupled with tracking of the intracellular fate of the nanoparticle delivery vehicle and its drug cargo. Here, we present a robust multifunctional liquid crystal NP (LCNP)-based delivery system that affords facile intracellular fate tracking coupled with the efficient delivery and modulation of the anticancer therapeutic doxorubicin (Dox), employed here as a model drug cargo. The LCNPs consist of (1) a liquid crystal cross-linking agent, (2) a homologue of the organic chromophore perylene, and (3) a polymerizable surfactant containing a carboxylate headgroup. The NP core provides an environment to both incorporate fluorescent dye for spectrally tuned particle tracking and encapsulation of amphiphilic and/or hydrophobic agents for intracellular delivery. The carboxylate head groups enable conjugation to biologicals to facilitate the cellular uptake of the particles. Upon functionalization of the NPs with transferrin, we show the ability to differentially label the recycling endocytic pathway in HEK 293T/17 cells in a time-resolved manner with minimal cytotoxicity and with superior dye photostability compared to traditional organic fluorophores. Further, when passively loaded with Dox, the NPs mediate the rapid uptake and subsequent sustained release of Dox from within endocytic vesicles. We demonstrate the ability of the LCNPs to simultaneously serve as both an efficient delivery vehicle for Dox as well as a modulator of the drug’s cytotoxicity. Specifically, the delivery of Dox as a LCNP conjugate results in a ∼40-fold improvement in its IC50 compared to free Dox in solution. Cumulatively, our results demonstrate the utility of the LCNPs as an effective nanomaterial for simultaneous cellular imaging, tracking, and delivery of drug cargos.

# Second Near-Infrared Conjugated Polymer Nanoparticles for Photoacoustic Imaging and Photothermal Therapy\_2018

Low photostability in aqueous solutions is the main drawback of synthetic photochromic dyes, which limits their switching performance and utility in biology, medicine, and life sciences. Even the most promising photochromes—reversibly photoswitchable diarylethenes (DAEs) with fluorescent “closed” forms—are known to undergo only several tens (typically 20–30) of switching cycles in aqueous solutions. In this work, we introduce water-soluble and highly photostable 1,2-[bis(2-ethyl/2-isobutyl-1-benzothiophene-1,1-dioxide-6-phenyl-3-yl)]perfluorocyclopentenes decorated with four −CONHC(CH2R)3 residues capped with 12 carboxylic acid groups (R = CH2CO2H, O(CH2)2CO2H). Under irradiation with UV (365 nm) and visible light (470 nm), they provide several hundred (for the “rapid” DAEs with isobutyl groups, up to 1000) full switching cycles in aqueous solutions without exclusion of air oxygen (outperforming the photoswitchable and fluorescent protein Dreiklang). The new branching approach based on secondary carboxamides with N-tert-alkyl residues decorated with polar groups may serve as a blueprint for the design of highly fatigue resistant and reversibly photoswitchable fluorescent probes applicable in life sciences as aqueous solutions.

# Multifunctional Liquid Crystal Nanoparticles for Intracellular Fluorescent Imaging and Drug Delivery\_2014

The fates of photochemically formed πσ\* states are one of the central issues in photobiology due to their significant contribution to the photostability of biological matter, formation of hydrated electrons, and the phenomenon of photoacidity. Nevertheless, our understanding of the underlying molecular mechanisms in aqueous solution is still incomplete. In this paper, we report on the results of nonadiabatic photodynamics simulations of microhydrated 2-aminooxazole molecule employing algebraic diagrammatic construction to the second order. Our results indicate that electron-driven proton transfer along H2O wires induces the formation of πσ\*/S0 state crossing and provides an effective deactivation channel. Because we recently have identified a similar channel for 4-aminoimidazole-5-carbonitrile [Szabla, R.; Phys. Chem. Chem. Phys. 2014, 16, 17617−17626], we conclude this mechanism may be quite common to all heterocyclic compounds with low-lying πσ\* states.

# Reversibly Photoswitchable Fluorescent Diarylethenes Resistant against Photobleaching in Aqueous Solutions\_2019

Two water-soluble near-infrared luminescent probes, which possess both conventional intense Stokes fluorescence and unique single-photon frequency upconversion luminescence (FUCL), were developed for sensitive and selective detection of pH changes in live cells. The water solubility and biocompatibility of these probes were achieved by introducing mannose residues through 2,2′-(ethylenedioxy)diethylamine tethered spacers to a near-infrared conventional fluorescence (CF) and FUCL organic fluorophore. At a pH higher than 7.4, the probes have ring-closed spirocyclic lactam structures, thus are colorless and nonfluorescent. Nevertheless, they sensitively respond to acidic pH values, with a drastic structural change to ring-opened spirocyclic lactam forms, which cause significant absorbance increases at 714 nm. Correspondingly, their near-infrared CF and FUCL intensities at 740 nm are also significantly enhanced when excited by 690 and 808 nm, respectively. The probes hold a variety of advantages such as high sensitivity, excellent reversibility and selectivity to pH over metal ions, low cellular autofluorescence background interference, good cell membrane permeability and photostability, as well as low cytotoxicity. Our results have successfully proven that these probes can visualize intracellular lysosomal pH changes in live cells by monitoring both near-infrared CF and FUCL changes.

# Luminescent Probes for Sensitive Detection of pH Changes in Live Cells through Two Near-Infrared Luminescence Channels\_2017

Photoelectrochemical (PEC) solar water splitting has received extensive attention because it promises to provide an alternative and sustainable source of energy. A key challenge is to achieve a stable PEC system in either acidic or basic electrolyte without degradation of the (photo)electrodes. We have used a cubic Cu2O film and porous granular bilayer Cu2O/CuO composite with a carbon protection layer as photocathode materials. The films were deposited under dif-ferent conditions, such as variation of the electrodeposition time, thermal oxidation of the Cu2O films in air vs. nitro-gen atmosphere and deposition of the carbon materials, and were investigated structurally and regarding their PEC performance. The optimized electrodes showed photocurrents up to 6.5 mA/cm-2 and 7.5 mA/cm-2 at potentials of 0 V and -0.1 V vs RHE at pH 5.5, respectively. The stabilities of the Cu2O/C and Cu2O/CuO/C photocathodes, at a low bias of 0.3 V vs RHE, were retained after 50 h. The strongly improved photostability of the photocathodes in comparison to electrodes in the absence of a carbon overlayer, is attributed to a more effective charge transfer and a protective role of carbon against photocorrosion.

# Efficient solar water splitting photocathodes comprising a copper oxide heterostructure protected by a thin carbon layer\_2019

Metal ion doping and nanocoating a CdS photocatalyst have been proven to be effective strategies to inhibit photocorrosion and improve photocatalytic performance. In this study, carbon-coated Cu+-doped CdS nanocomposites (C-Cu-CdS) with a stable petalous structure and highly uniform size distribution were successfully synthesized via a facile one-step solvothermal method. Both Cu+ doping and carbon coating to the CdS photocatalyst are realized in this one-step strategy. Benefiting from the unique core–shell structure and metal ion doping, the as-prepared C-Cu-CdS catalyst exhibits significantly enhanced photostability and visible-light-driven photocatalytic efficiency. For an optimal Cu+ doping percentage of 1.0%, an average hydrogen production rate of 2796 μmol h–1 g–1 and an apparent quantum efficiency of 16.0% at a wavelength of 420 nm was observed, the latter of which is nearly 9.3 times higher than that of the carbon-coated CdS product without Cu+ doping. The origin of the improved photocatalytic activity is systematically investigated by examining the effects of Cu+ doping.

# Electron-Driven Proton Transfer Along H2O Wires Enables Photorelaxation of πσ\* States in Chromophore–Water Clusters\_2015

Monomeric Kusabira Orange (mKO) is a green fluorescent protein (GFP)-like protein that emits orange light at a peak of 559 nm. We analyzed its X-ray structure at 1.65 Å and found a novel three-ring chromophore that developed autocatalytically from a Cys65-Tyr66-Glu67 tripeptide in which the side chain of Cys65 formed the third 2-hydroxy-3-thiazoline ring. As a result, the chromophore contained the C═NCOH group at the 2-position of the imidazolinone moiety such that the conjugated π-electron system of the chromophore was more extended than that of GFP but less extended than that of the Discosoma sp. red fluorescent protein (DsRed). Since a sulfur atom has potent nucleophilic character, the third 3-thiazoline ring is rapidly and completely cyclized. Furthermore, our structure reveals the presence of a π−π stacking interaction between His197 and the chromophore as well as a π−cation interaction between Arg69 and the chromophore. These structural findings are sufficient to account for the orange emission, pH tolerance, and photostability of mKO.

# One-Step Solvothermal Synthesis of Petalous Carbon-Coated Cu+-Doped CdS Nanocomposites with Enhanced Photocatalytic Hydrogen Production\_2017

We report the synthesis and characterization of highly luminescent colloidal nanocrystals consisting of CdSe cores protected with double inorganic shells (core−shell−shell nanocrystals). The outer ZnS shell provides efficient confinement of electron and hole wave functions inside the nanocrystal as well as high photochemical stability. Introducing the middle shell (CdS or ZnSe) sandwiched between CdSe core and ZnS outer shell allows considerable reducing strain inside nanocrystals because CdS and ZnSe have the lattice parameter intermediate to those of CdSe and ZnS. In contrast to CdSe/ZnS core−shells, in the core−shell−shell nanocrystals ZnS shell grows nearly defect free. Due to high quality of the ZnS shell, the core−shell−shell nanocrystals exhibit PL efficiency and photostability exceeding those of CdSe/ZnS nanocrystals. Preferential growth of the middle CdS shell in one crystallographic direction allows engineering the shape and luminescence polarization of the core−shell−shell nanocrystals.

# Structural Characterization of a Thiazoline-Containing Chromophore in an Orange Fluorescent Protein, Monomeric Kusabira Orange\_2008

The highly electron-deficient, β-octafluorinated meso-tetrakis(pentafluorophenyl)-porphyrin (H2F28TPP) was metalated with platinum to afford the oxidatively robust luminophore [PtF28TPP], and its X-ray structure shows that the porphyrin core exists in a slightly saddle-shaped conformation. The absorption spectrum of [PtF28TPP] in CH2Cl2 displays a near-UV Soret band (B) at 383 nm (ε = 2.85 × 105 dm3 mol-1 cm-1) and two visible Q(1,0) and Q(0,0) bands at 501 (ε = 1.45 × 104 dm3 mol-1 cm-1) and 533 (ε = 1.36 × 104 dm3 mol-1 cm-1) nm, respectively. These absorption bands of [PtF28TPP] are blue-shifted from those in [PtF20TPP] (390, 504, and 538 nm, respectively) and [PtTPP] (401, 509, and 539 nm, respectively). Excitation of [PtF28TPP] (complex concentration = 1.5 × 10-6 mol dm-3) in dichloromethane at the Soret or Q(1,0) or Q(0,0) band gave a phosphorescence with peak maximum at 650 nm (lifetime = 5.8 μs) and a weak shoulder at 712 nm. Both the emission lifetime and quantum yield vary with solvent polarity, and plots of τ versus EK and Φ versus EK (where EK is the empirical solvent polarity parameter based on the hypsochromic shift of the longest wavelength absorption of the [Mo(CO)4{(C5H4N)HCNCH2C6H5}] complex with increasing solvent polarity; see:  Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. Prog. Phys. Org. Chem.1981, 13, pp 485−630) show linear correlation, indicating that the emission is sensitive to the local environment/medium. Electrochemical studies on [PtF28TPP] by cyclic voltammetry showed no porphyrin-centered oxidation at potential ≤ 1.5 V versus Ag/AgNO3, demonstrating that [PtF28TPP] is more resistant toward oxidation than [PtF20TPP] (E1/2 = 1.33 V) and [PtTPP] (E1/2 = 0.97 V). The porphyrin-centered reduction of [PtF28TPP] occurs at −0.75 and −1.18 V, which is anodically shifted from those at −1.06 and −1.55 V in [PtF20TPP], and −1.51 V in [PtTPP], respectively. The excited-state reduction potential of [PtF28TPP] is estimated to be 1.49 V versus Ag/AgNO3. Over 97% of the emission intensity of [PtF28TPP] was retained after irradiation with a high power mercury arc lamp (500 W) for 14 h, compared to 90% and 12% for [PtF20TPP] and [PtTPP], respectively; hence, [PtF28TPP] exhibits superior photostability. Quenching of the emission of [PtF28TPP] by oxygen, alcohol, catechol, and butylamine reveals that [PtF28TPP] is an oxidatively robust material with medium-sensitive photoluminescence properties.

# CdSe/CdS/ZnS and CdSe/ZnSe/ZnS Core−Shell−Shell Nanocrystals\_2004

SUNLIGHT-DRIVEN NANOWIRE CATALYSTS  
Photocatalysts are expected to be key components of nanodevices for harvesting sunlight and converting it into usable energy. However, most photocatalysts work only in the UV or near-UV regions of the solar spectrum with limited efficiency. Xiangfeng Duan and coworkers at the University of California, Los Angeles, have now prepared three-component integrated nanowire devices that serve as stable, efficient photocatalysts over a broad range of the solar spectrum ( Nano Lett., DOI: 10.1021/nl101010m). In each device, a platinumsilicon photodiode is sandwiched between silver and platinum. The entire structure is encased in an insulating silicon oxide shell with only the silver and platinum ends exposed. This structure improves the system’s photostability and allows the researchers to optimize photoelectrochemical reactions. The devices have an average quantum efficiency of about 45% across the visible and near-infrared regions, and they are more stable than TiO 2 photocatalysts. The researchers used the devices to catalyze formation of formic ...

# Electronic Spectroscopy, Photophysical Properties, and Emission Quenching Studies of an Oxidatively Robust Perfluorinated Platinum Porphyrin\_2004

Solid-state quantum emitters are a mainstay of quantum nanophotonics as integrated single-photon sources (SPS) and optical nanoprobes. Integrating such emitters with active nanophotonic elements is desirable in order to attain efficient control of their optical properties, but it typically degrades the photostability of the emitter itself. Here, we demonstrate a tunable hybrid device that integrates state of the art lifetime-limited single emitters (line width ∼40 MHz) and 2D materials at subwavelength separation without degradation of the emission properties. Our device’s nanoscale dimensions enable ultrabroadband tuning (tuning range >400 GHz) and fast modulation (frequency ∼100 MHz) of the emission energy, which renders it an integrated, ultracompact tunable SPS. Conversely, this offers a novel approach to optical sensing of 2D material properties using a single emitter as a nanoprobe.

# CONCENTRATES\_2010

Phototherapy, as an important class of noninvasive tumor treatment methods, has attracted extensive research interest. Although a large amount of the near-infrared (NIR) phototherapeutic agents have been reported, the low efficiency, complicated structures, tedious synthetic procedures, and poor photostability limit their practical applications. To solve these problems, herein, a donor–acceptor–donor (D–A–D) type organic phototherapeutic agent (B-3) based on NIR aza-boron-dipyrromethene (aza-BODIPY) dye has been constructed, which shows the enhanced photothermal conversion efficiency and high singlet oxygen generation ability by simultaneously utilizing intramolecular photoinduced electron transfer (IPET) mechanism and heavy atom effects. After facile encapsulation of B-3 by amphiphilic DSPE–mPEG5000 and F108, the formed nanoparticles (B-3 NPs) exhibit the excellent photothermal stabilities and reactive oxygen and nitrogen species (RONS) resistance compared with indocyanine green (ICG) proved for theranostic application. Noteworthily, the B-3 NPs can remain outstanding photothermal conversion efficiency (η = 43.0%) as well as continuous singlet oxygen generation ability upon irradiation under a single-wavelength light. Importantly, B-3 NPs can effectively eliminate the tumors with no recurrence via synergistic photothermal/photodynamic therapy under mild condition. The exploration elaborates the photothermal conversion mechanism of small organic compounds and provides a guidance to develop excellent multifunctional NIR phototherapeutic agents for the promising clinical applications.

# Electrical Control of Lifetime-Limited Quantum Emitters Using 2D Materials\_2019

The metastatic spread of primary tumors to regional lymph nodes (LNs) is an important prognostic indicator for cancer staging and clinical therapy. Therefore, developing lymphatic mapping probes with improved accuracy and efficiency is of vital importance. Conjugated polymers (CPs) have been established as useful optical probes for sensitive biological and chemical detection. As a member of CPs family, polythiophene derivatives have drawn increasing attraction because of their superior photostability, signal amplification ability, and flexible structures for modification. In addition, these excellent properties allow the promising in vivo application to real-time LNs mapping. Here, we first reported a radiolabeled dual-modal probe based on the polythiophene derivative (99mTc-PTP) that was used for LNs mapping with high sensitivity and specificity by preoperative single-photon emission computed tomography imaging and intraoperative optical guidance. 99mTc-PTP exhibits an excellent radio-fluorescence guidance ability and a remarkable biocompatibility and holds great potential to be a powerful probe for noninvasive LNs mapping.

# Highly Stable and Multifunctional Aza-BODIPY-Based Phototherapeutic Agent for Anticancer Treatment\_2018

One of the most rapidly growing areas of physics and nanotechnology is concerned with plasmonic effects on the nanometer scale; these have applications in sensing and imaging technologies. Nanoplasmonic colloids such as Ag and Au have been attracting active interest, and there has been a recent explosion in the use of these metallic nanostructures to modify the spectral properties of fluorophores favorably and to enhance the fluorescence emission intensity. In this feature article, we summarize our work over a range of nanoplasmonics-assisted biological applications such as flow cytometry, immunoassays, cell imaging and bioassays where we use custom-designed plasmonic nanostructures (Ag and Au) to enhance fluorescence signatures. This fluorophore–metal effect offers unique advantages in providing improved photostability and enhanced fluorescence signals. We discuss the plasmonic enhancement of lanthanide fluorophores whose long and microsecond lifetimes offer the advantage of background-free fluorescence detection, but low photon cycling rates lead to poor brightness. We also show that plasmonic colloids are capable of enhancing the emission of fluorescent nanoparticles, including upconverting nanocrystals and lanthanide nanocomposites.

# Dual-Modal Probe Based on Polythiophene Derivative for Pre- and Intraoperative Mapping of Lymph Nodes by SPECT/Optical Imaging\_2018

Polyvinyl chloride has been modified by photochemical reactions in order to either produce a conductive polymer or to improve its light-stability. In the first case, the PVC plate was extensively photochlorinated and then degraded by UV exposure in N2. Total dehydrochlorination was achieved by a short Ar+ laser irradiation at 488 nm that leads to a purely carbon polymer which was shown to exhibit an electrical conductivity. In the second case, an epoxy-acrylate resin was coated onto a transparent PVC sheet and crosslinked by UV irradiation in the presence of both a photoinitiator and a UV absorber. This superficial treatment was found to greatly improve the photostability of PVC as well as its surface properties.

# Plasmonic Approach to Enhanced Fluorescence for Applications in Biotechnology and the Life Sciences\_2012

This paper reports the initial results of an original and simple method to elaborate flexible, self-standing, and thick luminescent films suitable for optical devices. PVP/Y3Ga5O12:Tb3+ nanocomposite films have been successfully achieved from a sol–gel derived Y3Ga5O12:Tb3+ powder and an alcoholic solution of poly-N-vinylpyrrolidone (PVP). The structural, morphological, and optical properties of these nanocomposite films have been studied and compared to those of a pristine PVP film and Y3Ga5O12:Tb3+ powder. The nanocomposite films were characterized by infrared and Raman spectroscopies as well as scanning and transmission electron microscopies (SEM and TEM) and demonstrated good dispersion of the phosphor particles within the polymer matrix via an alveolar mesostructure. The optical properties of these nanocomposites were fully characterized, and both their excitation and emission spectra and decay curves were recorded. Furthermore, photostability of the nanocomposite films and of the luminescent raw powder has been studied after exposure to an accelerated artificial photoageing at wavelengths higher than 300 nm. The elaboration process used is both tunable and applicable to a large variety of powders and polymers because it does not require any additive to form homogeneous and easily shapeable phosphor/polymer nanocomposites applicable in a large variety of optical devices such as solid-state-lighting.

# Photochemical Modifications of Poly(vinyl chloride)Conducting Polymers and Photostabilization\_1988

A series of coumarin dyes (NKX-2593, NKX-2807, and NKX-2883) with one or two -CN groups as electron acceptors were synthesized and applied as dye sensitizers for dye-sensitized solar cells. Compared with the dye containing one -CN group, linking one more -CN group to the π-conjugation bridge positively shifts the lowest unoccupied molecular orbital and thus red-shifts the maximum absorption band, harvesting more photons in the long-wavelength region for photoelectric conversion. Among the three dyes studied, NKX-2883 showed the best photovoltaic performance, yielding 7.6% power conversion efficiency using a volatile electrolyte and demonstrating good photostability under visible light soaking with 6% of power conversion efficiency for 1000 h using a nonvolatile electrolyte.

# Luminescent Nanocomposites Made of Finely Dispersed Y3Ga5O12:Tb Powder in a Polymer Matrix: Promising Candidates for Optical Devices\_2012

Cy5−avidin conjugate-bound silver nanoparticles were prepared as a fluorescence molecular reagent for the cell imaging. Compared with the metal-free avidin conjugate, the avidin−metal complex was observed to display a stronger emission intensity, shorter lifetime, and better photostability. The avidin−metal complexes were conjugated with the biotin-sites on the surfaces of PM1 cell lines, and the cell images were recorded using scanning confocal microscopy. It was noticed that the avidin−metal complexes bound on the cell surfaces could be identified as the isolated emission spots distinct from the cellular autofluorescence. The emission intensity over the cell image was increased with an increase of the number of avidin−metal complexes on the cell surface but the lifetime was decreased. A quantitative regression curve was achieved between the amount of avidin−metal complex on the cell surface and the emission intensity or lifetime over the entire cell image. On the basis of this curve, we expect to develop an approach that can be used to quantify the amount of target molecules on the cell surfaces using the cell intensity and lifetime images at the single cell level.

# Molecular Design of Coumarin Dyes for Stable and Efficient Organic Dye-Sensitized Solar Cells\_2008

Through the use of a rhodamine-appended chelate, bpy-Rho, a versatile strategy has been demonstrated to readily form mitochondria-targeting photosensitizers via the incorporation of a variety of luminescent transition-metal systems, M-Rho, such as Re(I), Ir(III), Pt(II), and Rh(III). The emission from the rhodamine singlet excited state and the transition-metal triplet excited state is partially quenched by the depopulation of them into the dark rhodamine triplet excited state. The generation of the triplet excited state of a rhodamine moiety endows the complexes with mitochondria-targeting photosensitizing ability to form singlet oxygen (1O2) for use as a photodynamic therapy (PDT) agent upon visible-light irradiation. The combination of the rhodamine organic dye and luminescent transition-metal centers in such hybrid systems exhibits the synergistic merits for the biological applications, including low dark cytotoxicity, selective tumor cell uptake, high molar absorptivity suitable for low-energy excitation in the visible region, and high photostability. The corresponding in vitro photocytotoxicity and in vivo photo-antitumor efficacy have also been studied to demonstrate the potential PDT application of M-Rho.

# Fluorescent Avidin-Bound Silver Particle: A Strategy for Single Target Molecule Detection on a Cell Membrane\_2008

Although possessing high activity for solar hydrogen production, exploring robust Cu2O-based photocatalysts remains a challenging task due to its intrinsic drawback of susceptible oxidation. Herein, we present a strategy to stabilize Cu2O by modulating the exposed facets and structural defects of TiO2. Both experimental characterizations and theoretical calculations proved that surface oxygen vacancies in 101-faceted TiO2 could create conducting channels for denoting electrons to Cu2O, mimicking the Z-scheme charge transfer in natural photosynthesis. Due to the defect-enhanced charge separation and the effective scavenging of oxidative holes in Cu2O, Cu2O/TiO2 heterostructures with exposed {101} facets and oxygen vacancies exhibited 251-fold increased activity for solar water splitting, together with unpredicted photostability. In contrast, defect-induced isolated states in the bulk of 001-faceted TiO2 led to the formation of Type II Cu2O/TiO2 junction with moderate photoactivity and poor stability. Thus, our work not only provides insights into the facet- and defect-dependent interfacial mechanism in heterostructured nanocatalysts but also opens up a promising avenue for developing high-performance noble-metal-free photocatalysts for energy conversion applications.

# Versatile Strategy To Generate a Rhodamine Triplet State as Mitochondria-Targeting Visible-Light Photosensitizers for Efficient Photodynamic Therapy\_2019

Functionalized polymers containing mesogenic, photosensitive, and fluorescent side groups were synthesized for all-in-one films with anisotropic absorption and emission. Aligned films were prepared by a two-step bulk-alignment procedure combining a photochemical step at room temperature and a thermal aligning step at temperatures of the mesophases. The irradiation with linearly polarized light results in small values of anisotropy via angular-selective photoreactions of cinnamates, stilbenes, and anthracene moieties. The photoinduced anisotropy was significantly amplified by annealing above the glass transition temperature of the liquid crystalline polymers, resulting in a cooperative alignment of all side groups leading to dichroism values up to 0.7 (dichroic ratio up to 6.7) and ratios of anisotropic fluorescence up to 8. The irradiation conditions for the induction of anisotropy were optimized concerning wavelength and dose with respect to the absorption of photosensitive groups and the limited photostability of the dyes. Depending on the distribution of the photoproducts, alignment parallel or perpendicular to the electric field vector of the incident light was induced in dependence on the polymer composition and irradiation conditions.

# Defect Modulation of Z-Scheme TiO2/Cu2O Photocatalysts for Durable Water Splitting\_2019

A blue fluorophore of Schiff base zinc complex is prepared by a hydrolysis-free solution-based synthetic method. Under ultraviolet (UV) excitation, the complex produces blue emission with a quantum yield (Q) of 42.6% in methylene chloride and 24.0% in standalone powder form. Quantum mechanical calculations show that the blue emission is generated by the change in the chemical state of the ligand associated with the complexation with Zn cations. Thin films of Zn complexes incorporated in polymethylmethacrylate (PMMA) and cellulose acetate butyrate (CAB) polymers are also prepared by dispersing the complexes into the polymer matrices. These hybrid polymer films exhibit several notable features, particularly enhanced luminescence efficiency (with maximum Q of 85.8% for PMMA and 30.0% for CAB) and scalability for fabrication over a large area while retaining the original properties of the host polymers. Light-emitting diodes are also fabricated using the CAB hybrid thin films, and they show a Q of 43.2% with excellent photostability. The complex and its hybrid films demonstrate their great potential for such applications as UV-to-blue conversion devices in photoelectronics, solar-cell concentrators, solid-state lighting and display, and greenhouse agriculture.

# Generation of Anisotropic Emission by Light-Induced Orientation of Liquid Crystalline Polymers\_2011

A plasmonic photocatalyst Ag−AgI supported on mesoporous alumina (Ag−AgI/Al2O3) was prepared by deposition−precipitation and photoreduction methods. The catalyst showed high and stable photocatalytic activity for the degradation and mineralization of toxic persistent organic pollutants, as demonstrated with 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and trichlorophenol (TCP) under visible light or simulated solar light irradiation. On the basis of electron spin resonance, cyclic voltammetry analyses under a variety of experimental conditions, two electron transfer processes were verified from the excited Ag NPs to AgI and from 2-CP to the Ag NPs, and the main active species of O2•− and excited h+ on Ag NPs were involved in the photoreaction system of Ag−AgI/Al2O3. A plasmon-induced photocatalytic mechanism was proposed. Accordingly, the plasmon-induced electron transfer processes elucidated the photostability of Ag−AgI/Al2O3. This finding indicates that the high photosensitivity of noble metal NPs due to surface plasmon resonance could be applied toward the development of new plasmonic visible-light-sensitive photocatalysts and photovoltaic fuel cells.

# Blue-Light-Emitting Photostable Hybrid Films for High-Efficiency Large-Area Light Converter and Photonic Applications\_2018

This study is to develop a method for preparing fluorescent microspheres with steady and strong fluorescence as well as the surface functionality for bioconjugation. Layer-by-layer technique was employed to introduce poly(phenylenevinylene) (PPV) precursor, diazoresin (DAR), and polyanion, including poly(acrylic acid) (PAA) and poly(sodium-p-styrenesulfonate) (PSS), onto the substrate polystyrene-divinylbenzene microspheres with sulfonic groups on the surface (SPSDVB). The conversion of PPV precursor into fluorescent PPV as well as the cross-linking reaction between DAR and polyanion, were accomplished simultaneously in the following thermal treatment. After optimizing the DAR concentration, the selection of polyelectrolytes and the coating sequence, the cross-linked multilayer coated PPV microspheres, SPSDVB-(PPV/PSS/DAR/PAA) spheres, were prepared. These spheres were found to have uniform size with a clear core–shell structure and display even and strong fluorescence, based on the characterization by flow cytometry, microscopy, and photophysics. They were found to be stable and highly resistant to common solvents and even “dissociation agent”, as well as possess good thermal stability and photostability. The feasibility of conjugating biomolecules on the surface of spheres was also demonstrated.

# Plasmon-Induced Photodegradation of Toxic Pollutants with Ag−AgI/Al2O3 under Visible-Light Irradiation\_2009

Chemotherapeutic agents with low toxicity to normal tissues are a major goal in cancer research. In this regard, the therapeutic activities of cationic dyes, such as rhodamine 6G, toward cancer cells have been studied for decades with observed toxicities toward normal and cancer cells. Herein, we report rhodamine 6G-based organic salts with varying counteranions that are stable under physiological conditions, display excellent fluorescence photostability, and more importantly have tunable chemotherapeutic properties. Our in vitro studies indicate that the hydrophobic compounds of this series allow production of nanoparticles which are nontoxic to normal cells and toxic to cancer cells. Furthermore, the anions, in combination with cations such as sodium, were observed to be nontoxic to both normal and cancer cells. To the best of our knowledge, this is the first demonstration that both the cation and anion play an extremely important and cooperative role in the antitumor properties of these compounds.

# Preparation of Cross-Linked, Multilayer-Coated Fluorescent Microspheres with Functional Groups on the Surface for Bioconjugation\_2015

Stimuli-triggered nanoplatforms have become attractive candidates for combined strategies for advanced liver cancer treatment. In this study, we designed a light-responsive nanoplatform with folic acid-targeting properties to surmount the poor aqueous stability and photostability of indocyanine green (ICG). In this Janus nanostructure, ICG was released on-demand from mesoporous silica compartments in response to near-infrared (NIR) irradiation, exhibiting predominant properties to convert light to heat in the cytoplasm to kill liver cancer cells. Importantly, the silver ions released from the silver compartment that were triggered by light could induce efficient chemotherapy to supplement photothermal therapy. Under NIR irradiation, ICG-loaded Janus nanoplatforms exhibited synergistic therapeutic capabilities both in vitro and in vivo compared with free ICG and ICG-loaded mesoporous silica nanoparticles themselves. Hence, our Janus nanoplatform could integrate ICG-based photothermal therapy and silver ion-based chemotherapy in a cascade manner, which might provide an efficient and safe strategy for combined liver cancer therapy.

# Tunable Cytotoxicity of Rhodamine 6G via Anion Variations\_2013

By introducing an 18 nm thick Au nanofilm, selective enhancement of green emission from lanthanide-doped (β-NaYF4:Yb3+/Er3+) upconversion nanoparticles (UCNPs) is demonstrated. The Au nanofilm is deposited on a microfiber surface by the sputtering method and then covered with the UCNPs. The plasma on the surface of the Au nanofilm can be excited by launching a 980 nm wavelength laser beam into the microfiber, resulting in an enhancement of the local electric field and a strong thermal effect. A 36-fold luminescence intensity enhancement of the UCNPs at 523 nm is observed, with no obvious reduction in the photostability of the UCNPs. Further, the intensity ratios of the emissions at 523–545 nm and at 523–655 nm are enhanced with increasing pump power, which is attributed to the increasing plasmon-induced thermal effect. Therefore, the fabricated device is further demonstrated to exhibit an excellent ability in temperature sensing. By controlling the pump power and the UCNP concentration, a wide temperature range (325–811 K) and a high temperature resolution (0.035–0.046 K) are achieved in the fabricated device.

# Janus Silver/Silica Nanoplatforms for Light-Activated Liver Cancer Chemo/Photothermal Therapy\_2017

To obtain highly efficient blue–violet light conversion agents used for an agricultural film, six triarylacrylonitrile derivatives and their doping films were prepared. Further, the luminogens have the ability to convert ultraviolet light into blue–violet light and exhibit aggregation-dependent fluorescence emission and high-contrast fluorescence quantum yields from 0.004 to 0.833. On the basis of X-ray single-crystal diffraction analysis and aggregation-induced emission activity tests, the variant fluorescence quantum yields are attributed to intermolecular π–π stacking and phase transition between the crystalline state and amorphous state. In a simulated greenhouse environment, the luminogens exhibit excellent photostability. However, their fluorescence intensity drops to 17–40% of the prime intensity after outdoor radiation for 1 month as a result of the ring-closing oxidation reaction (in the summer). By comprehensively considering the above photophysical properties and mechanical properties of the doping film, 2-([1,1′-biphenyl]-4-yl)-3,3-diphenylacrylonitrile is a potential light conversion agent for an agricultural film in the winter. More importantly, the results indicate that the properties of the light conversion films are expected to be further improved by molecular design, inhibiting the ring-closing oxidation reaction and dispersion of crystalline nanoparticles in the doping film.

# Plasmon-Induced Selective Enhancement of Green Emission in Lanthanide-Doped Nanoparticles\_2017

New indicators for optical CO2 sensors are synthesized in two steps from the commercially available diketo-pyrrolo-pyrrole (DPP) pigments Irgazin Ruby and Irgazin Scarlet. After introduction of bis(2-ethylhexyl) sulfonamide groups via a simple two-step synthesis, the pigments are rendered highly soluble in organic solvents and in polymers and show pH-dependent absorption and emission spectra. The new indicators have molar absorption coefficients in a 20 000–50 000 M–1 cm–1 range, possess quantum yields close to unity, and feature good photostability. The indicators along with a quaternary ammonium base are embedded into ethyl cellulose to give optical carbon dioxide sensors. The absorption and emission spectra of the deprotonated form are bathochromically shifted by more than 100 nm compared to the neutral form (λmax absorption 496–550 nm; λmax emission 564–587 nm). This enables colorimetric read-out and self-referenced ratiometric fluorescence intensity measurements. Importantly, the dynamic range of the sensors based on the new indicators is significantly different (0–10 kPa and 1–100 kPa CO2) that enables a broad variety of applications.  
New DPP dyes are conveniently prepared from commercially available pigments and represent a new class of colorimetric and fluorescent pH indicators for optical carbon dioxide sensors.

# Exploration of Highly Efficient Blue–Violet Light Conversion Agents for an Agricultural Film Based on Structure Optimization of Triphenylacrylonitrile\_2018

Chemical doping with heteroatoms can effectively modulate physicochemical and photochemical properties of carbon dots (CDs). However, the development of multi heteroatoms codoped carbon nanodots is still in its early stage. In this work, a facile hydrothermal synthesis strategy was applied to synthesize multi heteroatoms (nitrogen and phosphorus) codoped carbon nanodots (N,P-CDs) using glucose as carbon source, and ammonia, phosphoric acid as dopant, respectively. Compared with CDs, the multi heteroatoms doped CDs resulted in dramatic improvement in the electronic characteristics and surface chemical activities. Therefore, the N,P-CDs prepared as described above exhibited a strong blue emission and a sensitive response to Fe3+. The N,P-CDs based fluorescent sensor was then applied to sensitively determine Fe3+ with a detection limit of 1.8 nM. Notably, the prepared N,P-CDs possessed negligible cytotoxicity, excellent biocompatibility, and high photostability. It was also applied for label-free detection of Fe3+ in complex biological samples and the fluorescence imaging of intracellular Fe3+, which indicated its potential applications in clinical diagnosis and other biologically related study.

# Diketo-Pyrrolo-Pyrrole Dyes as New Colorimetric and Fluorescent pH Indicators for Optical Carbon Dioxide Sensors\_2013

Polymer solar cells (PSCs) have achieved power conversion efficiencies exceeding 10%, but their performance has been limited under concentrated sunlight because of poor stability and recombination processes despite their potential for low-cost concentrated solar power. Recently, ternary polymer solar cell blends have been explored as a strategy to improve PSC performance; however, this approach has been demonstrated only for polymer–fullerene solar cells with organic ternary additives and has not addressed stability issues under supersolar irradiation. Here, we present the first polymer solar cells comprising ternary blends of high efficiency polymers, nonfullerene perylenediimide acceptors, and semiconducting single-walled carbon nanotube additives. We find that the addition of carbon nanotubes reduces efficiency-degrading recombination and improves performance and photostability, most notably under concentrated sunlight exceeding 10 suns. The utilization of carbon nanomaterials as ternary additives in organic photovoltaics creates new opportunities for integrating solution-processed solar cells with energy conversion systems based on solar concentrators.

# Nitrogen and Phosphorus Co-Doped Carbon Nanodots as a Novel Fluorescent Probe for Highly Sensitive Detection of Fe3+ in Human Serum and Living Cells\_2016

The excellent optical properties of quantum dots (QDs), such as high brightness, high photostability, continuous absorption, and narrow emission bandwidth, make them ideal as optical labels to develop QD-based immunohistofluorescence (IHF) imaging for multiplexing cancer biomarker detection on formalin-fixed and paraffin-embedded (FFPE) tissues. IHF is very important for the prediction of a patient’s response to cancer chemotherapy or radiotherapy. QD-based IHF faces several challenges that differ from those encountered by organic dye based IHF for clinical assays. The current work addresses some of these issues. Initially, the chemical stability of QDs and organic dyes were compared. The results showed that QDs were stable for at least 5 months on FFPE tissue, whereas organic dyes were photobleached shortly after exposure to light. Various staining methods were also studied. QD fluorescence intensity on the tissue stained with primary antibody (Ab, p16, survivin, EF1α) conjugated QDs from our company was comparable to the signal from a commercially available method in which the tissue was stained with a primary p16 Ab and a QD-labeled secondary goat anti mouse Ab respectively. Finally, the effect of the amount of Ab conjugated to QD on tissue imaging was also studied. There was no significant increase in the QD fluorescence signal on tissues when the Ab:QD ratio increased from 5 to 30. In addition, protein G was tested as an adaptor protein to link Ab to QDs for IHF staining. However, the proper blocking of the protein G on QDs was necessary to reduce crosstalk. The biomarker quantification in QD-based IHF was validated by conventional Western blot and immunohistochemistry. The results contained herein demonstrate a promising application of QDs in multiplex detection and quantification of biomarkers.

# Ternary Polymer–Perylenediimide–Carbon Nanotube Photovoltaics with High Efficiency and Stability under Super-Solar Irradiation\_2016

Conjugated polymers (CPs) have drawn growing attention in cancer phototherapy and imaging due to their large extinction coefficients, robust photostability, and good biocompatibility. Herein, we propose a new type of photothermal therapy materials on the basis of BODIPY-diketopyrrolopyrrole CPs, where the number of methyl substituents at the β and β′ positions on BODIPYs is variable, allowing us to investigate the interplay between the structure of the monomers and the related properties of CPs. Combining the experimental data with theoretical calculations, we concluded that with the decrease of the number of methyl moieties on the β and β′ positions of BODIPY, the polymerization degree and the solubility of the obtained CPs improved and the polymeric spatial planarization and degrees of conjugation increased, inducing the bathochromic shift of absorption, which resulted in the absorption spectra getting closer to the near-infrared region and more conducive to the application of the conjugated polymers in vivo. Afterward, the CP nanoparticles were constructed and their photothermal activity in cancer therapy was validated by a series of in vitro and in vivo experiments. In this paper, we provide a new way to manipulate properties of CPs with great potential in photothermal therapy through structural engineering.

# Quantum Dot-Based, Quantitative, and Multiplexed Assay for Tissue Staining\_2013

Development of visible-light photocatalytic materials is an ultimate goal for solar-driven CO2 conversion. Au nanoclusters (NCs) may potentially serve as components for harvesting visible light but can hardly perform solar-driven CO2 reduction due to the lack of catalytic sites. Herein, we report an effective strategy for turning Au nanoclusters catalytically active for visible-light CO2 reduction, in which metal cations (Fe2+, Co2+, Ni2+, and Cu2+) are grafted to the Au NCs using l-cysteine as a bridging ligand. The metal–S bonding bridge facilitates the electron transfer from Au NCs to metal cations so that the grafted metal cations can receive photoinduced electrons and work as catalytic sites for CO2 reduction. The varied d-band centers and binding energies with CO2 for different metal cations allow tuning electron transfer efficiency and CO2 activation energy. Furthermore, the photostability of Au NCs-based catalyst can be significantly enhanced through the encapsulation with metal–organic frameworks. This work opens a new door for the photocatalyst design based on metal clusters and sheds light on the surface engineering of metal clusters toward specific applications.

# Rational Design of BODIPY-Diketopyrrolopyrrole Conjugated Polymers for Photothermal Tumor Ablation\_2019

Carbon dots (CDs) are a new class of photoluminescent (PL), biocompatible, environment-friendly, and low-cost carbon nanomaterials. Synthesis of highly efficient red-emitting carbon dots (R-CDs) on a gram scale is a great challenge at present, which heavily restricts the wide applications of CDs in the bioimaging field. Herein, R-CDs with a high quantum yield (QY) of 53% are produced on a gram scale by heating a formamide solution of citric acid and ethylenediamine. The as-prepared R-CDs have an average size of 4.1 nm and a nitrogen content of about 30%, with an excitation-independent emission at 627 nm. After detailed characterizations, such strong red fluorescence is ascribed to the contribution from the nitrogen- and oxygen-related surface states and the nitrogen-derived structures in the R-CD cores. Our R-CDs show good photostability and low cytotoxicity, and thus they are excellent red fluorescence probes for bioimaging both in vitro and in vivo.

# Turning Au Nanoclusters Catalytically Active for Visible-Light-Driven CO2 Reduction through Bridging Ligands\_2018

We have developed a simple method to prepare bright and photostable luminescent silica nanoparticles of different sizes and narrow size distribution in high yield. The method is based on the use of Stöber synthesis in the presence of a fluorophore to form bright silica nanoparticles. Unlike micro-emulsion-based methods often used to prepare luminescent silica particles, the Stöber method is a one-pot synthesis that is carried out at room temperature under alkaline conditions in ethanol:water mixtures and avoids the use of potentially toxic organic solvents and surfactants. Our luminescent particles contained the transition metal complex tris(1,10-phenanthroline) ruthenium(II) chloride, [Ru(phen)3]Cl2. They showed higher photostability and a longer fluorescence lifetime compared to free Ru(phen)3 solutions. Leakage of dye molecules from the silica particles was negligible, which was attributed to strong electrostatic attractions between the positively charged ruthenium complex and the negatively charged silica. To demonstrate the utility of the highly luminescent silica nanoparticles in bioassays, we further modified their surface with streptavidin and demonstrated their binding to biotinylated glass slides. The study showed that digital counting of the luminescent nanoparticles could be used as an attractive alternative to detection techniques involving analogue luminescence detection in bioanalytical assays.

# Highly Efficient Red-Emitting Carbon Dots with Gram-Scale Yield for Bioimaging\_2017

The spatial resolution and fluorescence signal amplitude in stimulated emission depletion (STED) microscopy is limited by the photostability of available fluorophores. Here, we show that negatively charged silicon vacancy (SiV) centers in diamond are promising fluorophores for STED microscopy, owing to their photostable, near-infrared emission and favorable photophysical properties. A home-built pulsed STED microscope was used to image shallow implanted SiV centers in bulk diamond at room temperature. The SiV stimulated emission cross section for 765–800 nm light is found to be (4.0 ± 0.3) × 10–17 cm2, which is approximately 2–4 times larger than that of the negatively charged diamond nitrogen vacancy center and approaches that of commonly used organic dye molecules. We performed STED microscopy on isolated SiV centers and observed a lateral full-width-at-half-maximum spot size of 89 ± 2 nm, limited by the low available STED laser pulse energy (0.4 nJ). For a pulse energy of 5 nJ, the resolution is expected to be ∼20 nm. We show that the present microscope can resolve SiV centers separated by ≲150 nm that cannot be resolved by confocal microscopy.

# Stöber Synthesis of Monodispersed Luminescent Silica Nanoparticles for Bioanalytical Assays\_2005

In this study, fluorescent metal nanoshells were synthesized as a molecular imaging agent to detect single microRNA (miRNA) molecules in the cells positive to lung cancer. These metal nanoshells were composed of silica spheres with encapsulated Ru(bpy)32+ complexes as cores and thin silver layers as shells. Compared with the silica spheres in the absence of metal, the metal nanoshells displayed an enhanced emission intensity, shortened lifetime, and extended photostability. The single-stranded probe oligonucleotides were covalently bound on the metal nanoshells to hybridize with the target miRNA-486 molecules in the cells. It was shown that with stronger emission intensity and longer lifetime, the conjugated metal nanoshells were isolated distinctly from the cellular autofluorescence on the cell images. These emission spots on the cell images were counted accurately and analyzed with a pool of cells representing the miRNA-486 expression levels in the cells. The results may reflect a genomic signal change and provide a reference to lung cancer early diagnosis as well as other diseases.

# Stimulated Emission Depletion Microscopy with Diamond Silicon Vacancy Centers\_2019

This paper reports on the production of Langmuir films of regioregular poly(3-hexylthiophene) (P3HT) and their characterization by surface pressure isotherms and UV–vis in situ spectroscopy aiming at the best spreading conditions. Hybrid films containing the polymer and gold nanoparticles were obtained through the use of the optimized parameters for neat P3HT. Two types of hybrid films with P3HT and gold nanoparticles were studied. In the first type, gold nanoparticles in an aqueous solution were used in a subphase of a Langmuir trough and the polymer spread on the air/water interface. In the second type, 1-octadecanethiol capped gold nanoparticles (AuNpOctathiol) were used in a mixture with P3HT in chloroform and spread on the air–water interface. The Langmuir films were transferred to several solid substrates by the Langmuir–Schaefer (LS) method. The surface morphology was characterized by Scanning Electron Microscopy with Field Emission Guns (SEM-FEG), and the presence of gold nanoparticles in the films was confirmed. The growth of the layers in the films was monitored by transmission UV–vis spectroscopy, and the existence of optical anisotropy was investigated by polarized UV–vis spectroscopy. The results imply that the polymer backbone adopts a preferential orientation during the compression, which has a strong component parallel to the trough barrier, and is influenced by the presence of the nanoparticles in the films. The photostability of the films was studied by their exposition to a white light, and the hybrid films formed with P3HT and AuNpOctathiol showed an increase in the photostability, in comparison to the neat P3HT. Such an increase indicates that somehow the AuNpOctathiol molecules provide some protection against the photodegradation of P3HT.

# Fluorescent Metal Nanoshell Probe to Detect Single miRNA in Lung Cancer Cell\_2010

Fluorescent organic nanoparticles have a much better photostability than molecule-based probes. Here, we report a simple strategy to detect chemicals and biomolecules by a binary nanoparticle system based on fluorescence resonance energy transfer (FRET). Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO, energy donor) and poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, energy acceptor) are utilized to prepare the binary nanoparticle system through a reprecipitation method. Since the FRET process is strongly distance-dependent, a change in the interparticle distance between the two kinds of nanoparticles after introduction of analytes will alter the FRET efficiency. The response of the binary nanoparticle system to cationic polyelectrolytes was investigated by monitoring the FRET efficiency from PFO to MEH-PPV nanoparticles and the fluorescence color of the nanoparticle solutions. Furthermore, the cationic polyelectrolyte pretreated binary nanoparticle system can be used to detect DNA by desorption of nanoparticles from the polyelectrolyte’s chains and the detection concentration can go down to 10–14 M. Thus, the binary nanoparticle system shows great promise for applications in chemical sensing or biosensing.

# Langmuir and Langmuir–Schaefer Films of Poly(3-hexylthiophene) with Gold Nanoparticles and Gold Nanoparticles Capped with 1-Octadecanethiol\_2014

We have developed a facile and easily accessible layer-by-layer (LBL) self-assembly route to synthesize hierarchically ordered M/TNTs (M = Au, Ag, Pt) heterostructures. These integrated heterostructures show remarkably enhanced photoactivity and outstanding photostability; photoelectrochemical exploitations substantiated the contribution role of metal NPs acting as “electron reservoir” in prolonging the lifetime of photogenerated electron–hole charge carriers. In addition, these well-defined self-assembled hybrid systems can also be used as a promising catalyst for recycled selective catalytic reduction of 4-nitrophenol toward 4-aminophenol. The integration of high photoactivity and efficient catalytic reduction properties of the heterostructures lies crucially on the LBL self-assembly-induced monodispersivity of metal NPs on the framework of TNTs, and, particularly, the intimate interfacial contact between metal NPs and TNTs substrate arising from the pronounced electrostatic attractive interaction afforded by polyelectrolytes multilayering. Our results show that the design and utilization of highly ordered metal/1-D semiconductor hybrid nanostructures based on the facile LBL self-assembly strategy can find diverse catalytic applications.

# Fluorescence Resonance Energy Transfer in a Binary Organic Nanoparticle System and Its Application\_2015

Luminescent solar concentrators (LSCs) show promise because of their potential for low-cost, large-area, and high-efficiency energy harvesting. Stokes shift engineering of luminescent quantum dots (QDs) is a favorable approach to suppress reabsorption losses in LSCs; however, the use of highly toxic heavy metals in QDs constitutes a serious concern for environmental sustainability. Here, we report LSCs based on cadmium-free InP/ZnO core/shell QDs with type-II band alignment that allow for the suppression of reabsorption by Stokes shift engineering. The spectral emission and absorption overlap was controlled by the growth of a ZnO shell on an InP core. At the same time, the ZnO layer also facilitates the photostability of the QDs within the host matrix. We analyzed the optical performance of indium-based LSCs and identified the optical efficiency as 1.45%. The transparency, flexibility, and cadmium-free content of the LSCs hold promise for solar window applications.

# Layer-by-Layer Self-Assembly Construction of Highly Ordered Metal-TiO2 Nanotube Arrays Heterostructures (M/TNTs, M = Au, Ag, Pt) with Tunable Catalytic Activities\_2012

We developed a metal-enhanced fluorescence (MEF) substrate by modification of the commercially available surface-enhanced Raman spectroscopy (SERS) substrate that may meet the reproducibility and sensitivity challenge of MEF. In spite of many studies and interest in MEF from a number of research groups, application to real-world situations and its commercial use remain challenging mainly due to the difficulties in fabricating reproducible MEF substrates. Specifically, one of the challenges is achieving a standardized MEF substrate for reproducible fluorescence intensity enhancement and/or changes in lifetime. The gold standard klarite substrates for SERS were coated with a thin layer of silver nanoparticles for MEF studies. To test the newly developed MEF substrates, a monolayer of streptavidin conjugated Alexa-647 was assembled on biotinylated glass or MEF substrates. We observed over 50-fold increase in the fluorescence intensity from a monolayer of streptavidin conjugated Alexa-647 on the biotinylated MEF substrate compared to the same on glass substrate. A significant reduction in the lifetime and increased photostability of Alexa-647 on MEF substrate were observed. Fluorescence lifetime imaging was performed on the monolayer of dye assembled on the modified SERS substrates. We expect this study will serve as a platform to encourage the future use of a standardized MEF substrate for a plethora of sensing applications.

# Highly Emissive AIEgens with Multiple Functions: Facile Synthesis, Chromism, Specific Lipid Droplet Imaging, Apoptosis Monitoring, and In Vivo Imaging\_2018

Fluorescent organic nanoparticles have a much better photostability than molecule-based probes. Here, we report a simple strategy to detect chemicals and biomolecules by a binary nanoparticle system based on fluorescence resonance energy transfer (FRET). Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO, energy donor) and poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, energy acceptor) are utilized to prepare the binary nanoparticle system through a reprecipitation method. Since the FRET process is strongly distance-dependent, a change in the interparticle distance between the two kinds of nanoparticles after introduction of analytes will alter the FRET efficiency. The response of the binary nanoparticle system to cationic polyelectrolytes was investigated by monitoring the FRET efficiency from PFO to MEH-PPV nanoparticles and the fluorescence color of the nanoparticle solutions. Furthermore, the cationic polyelectrolyte pretreated binary nanoparticle system can be used to detect DNA by desorption of nanoparticles from the polyelectrolyte’s chains and the detection concentration can go down to 10–14 M. Thus, the binary nanoparticle system shows great promise for applications in chemical sensing or biosensing.

# Metal-Enhanced Fluorescence Lifetime Imaging and Spectroscopy on a Modified SERS Substrate\_2013

Novel N-aryl-substituted 2-borylbenzaldimines 6 and related systems with extended π-framework 7 based on two borylbenzaldimine units linked by a spacer moiety were synthesized by condensation reactions of 2-(dimesitylboryl)benzaldehyde 3 with various amines 4 and diamines 5. All compounds were completely characterized including X-ray diffraction, especially in view of Lewis acid–base B–O and B–N interactions. The electronic as well as the photophysical properties of bisimines 7 were determined using cyclic voltammetry, UV/vis, and fluorescence spectroscopy and quantum chemistry. These compounds feature large Stokes shifts and reversible reduction waves. Interestingly, UV irradiation experiments unfold enhanced photostability for compounds 7 with an extended π-skeleton. By use of 1,8-diaminonaphthalene we observed the formation of a hitherto unknown BN-heterocyclic compound 9 fused with a perimidine skeleton. Structural and energetic aspects were evaluated by high level quantum chemical methods (DFT and SCS-MP2-calculations).

# Synthesis and Photophysical Properties of Aryl-Substituted 2-Borylbenzaldimines and Their Extended π-Conjugated Congeners\_2012

Large two-photon absorption cross section and high fluorescence quantum yield (QY) of a fluorescent probe is highly desirable to achieve high resolution in two-photon excited fluorescence imaging. Taking poly(9,9-dihexylfluorene-alt-2,1,3-benzothiadiazole) (PFBT) as an example, we report a one-step approach to synthesize PFBT loaded nanoparticles (NPs) with both large two-photon absorption cross section and high fluorescence QY in aqueous media through a micelle and silica coprotection strategy. The PFBT loaded NPs show a two-photon absorption cross section of 1085 GM at 810 nm based on polymer chain concentration and an emission maximum at 545 nm with a high fluorescence QY of 75%. The fluorescence lifetime investigation reveals that the high fluorescence QY is mainly due to reduced polymer aggregation and minimized environment influence on conjugated polymer (CP) fluorescence quenching. The synthesized PFBT NPs have shown good colloid stability and photostability as well as benign biocompatibility, which have been further applied to visualize the mouse brain vasculature through intravital two-photon excited brain vascular imaging with high contrast. The developed micelle/silica coprotection strategy should be generally applicable to other CP NPs with improved brightness and stability for various biological applications.

# Stokes-Shift-Engineered Indium Phosphide Quantum Dots for Efficient Luminescent Solar Concentrators\_2018

In this article, a simple protocol to prepare water-soluble fluorescent copper nanoclusters (CuNCs) using trypsin as a stabilizer and hydrazine hydrate as a reducing agent was reported. It was found that the pH of the reaction solution was critical in determining the fluorescence of CuNCs. CuNCs with blue and yellow fluorescent emission were obtained under basic and acidic conditions, respectively. Although the detailed formation mechanisms of these CuNCs required further analysis, the synthetic route was promising for preparing different fluorescent metal NCs for applications. With good water solubility and excellent photostability, the yellow-emitting CuNCs could serve as a fluorescence probe for detection of Hg2+ based on the aggregation-induced quenching mechanism. The fluorescence quenching efficiency had fantastic linearity to Hg2+ concentrations in the range of 0.1–100 μM, with a limit of detection of 30 nM. Additionally, the yellow-emitting CuNCs exhibited negligible cytotoxicity and were successfully applied to bioimaging of HeLa cells.

# Micelle/Silica Co-protected Conjugated Polymer Nanoparticles for Two-Photon Excited Brain Vascular Imaging\_2014

The stability of fluorene-based compounds and polymers, especially at the bridged C-9 position under photoirradiation and thermal treatment, has claimed wide attention. We report the electronic, vibrational, and MALDI-TOF mass spectral combined studies for the fluorene oligomers with alkyl and aromatic substitutions under UV-light irradiation. The low-energy emission and the formation of ketonic defects after degradation highly depend on the proportion of alkyl substitution. The oligomer with fully aromatic substitution shows good stability, but when the proportion of alkyl substitution increases, their photostability rapidly decreases. The mass spectra show not only the mass of the fluorenone−fluorene trimer but also another new degradation product with a large mass (pristine oligomer plus 14) from alkyl oxidation, which testify to the assistance of alkyl side chain during degradation. We propose that the degradation of fluorene is a radical chain process propagated by alkyl side chains, and then the different stability between alkyl and aromatic substitution can be well explained.

# pH-Regulated Synthesis of Trypsin-Templated Copper Nanoclusters with Blue and Yellow Fluorescent Emission\_2017

Mesoporous silicon (PSi) has been shown to have extensive application opportunities in biomedicine, whereas it has frequently failed to produce complex systems based on PSi due to the lack of surface functional groups or the instability of the unmodified PSi surface. In the present study, PSi nanoparticles, stabilized by thermal oxidation or thermal carbonization, were successfully modified by grafting aminosilanes on the surface. The modifications were performed by covalently bonding 3-triethoxysilylpropylamine (APTES) or 3-(2-aminoethylamino) propyldimethoxymethylsilane (AEAPMS) on thermally oxidized PSi (TOPSi) and thermally carbonized PSi (TCPSi). These materials were systematically characterized with N2 ad/desorption, TEM, contact angle, zeta potential, FT-IR, 29Si CP/MAS NMR, and elemental analysis. To evaluate their application potentials, a fluorescent dye, fluorescein 5-isothiocyanate (FITC), was coupled on the surface of amine-modified nanoparticles. The effects of PSi matrix and surface amino groups on FITC coupling efficiency, fluorescent intensity, and the stability of fluorescence in simulated body fluid (SBF) were investigated. The nanoparticles modified with AEAPMS had higher FITC coupling efficiency than those modified with APTES. FITC-coupled TOPSi nanoparticles also possessed brighter fluorescence and better fluorescent stability in SBF. Furthermore, due to the protection caused by the mesoporous structure of PSi nanoparticles, the FITC-coupled TOPSi nanoparticles showed superior photostability in photobleaching experiment.

# Photodegradation of Polyfluorene and Fluorene Oligomers with Alkyl and Aromatic Disubstitutions\_2006

A near-neutral pH near-infrared (NIR) fluorescent probe utilizing a fluorophore-spacer- receptor molecular framework that can modulate the fluorescence emission intensity through a fast photoinduced electron-transfer process was developed. Our strategy was to choose tricarbocyanine (Cy), a NIR fluorescent dye with high extinction coefficients, as a fluorophore, and 4′-(aminomethylphenyl)-2,2′:6′,2′′-terpyridine (Tpy) as a receptor. The pH titration indicated that Tpy-Cy can monitor the minor physiological pH fluctuations with a pKa of ∼7.10 near physiological pH, which is valuable for intracellular pH researches. The probe responds linearly and rapidly to minor pH fluctuations within the range of 6.70−7.90 and exhibits strong dependence on pH changes. As expected, the real-time imaging of cellular pH and the detection of pH in situ was achieved successfully in living HepG2 and HL-7702 cells by this probe. It is shown that the probe effectively avoids the influence of autofluorescence and native cellular species in biological systems and meanwhile exhibits high sensitivity, good photostability, and excellent cell membrane permeability.

# Amine Surface Modifications and Fluorescent Labeling of Thermally Stabilized Mesoporous Silicon Nanoparticles\_2012

The excited states of UV-B absorber (4-methylbenzylidene)camphor (MBC) have been studied through measurements of UV absorption, phosphorescence, triplet–triplet (T–T) absorption, and steady-state and time-resolved electron paramagnetic resonance spectra in ethanol. The energy level and lifetime of the lowest excited triplet (T1) state of MBC were determined. The energy level of the T1 state of MBC is much lower than that of photolabile 4-tert-butyl-4′-methoxydibenzoylmethane. The weak phosphorescence and strong time-resolved EPR signals, and T–T absorption band of MBC were observed. These facts suggest that the significant proportion of the lowest excited singlet (S1) molecules undergoes intersystem crossing to the T1 state and the deactivation process from the T1 state is predominantly radiationless. The quantum yields of singlet oxygen production by MBC determined by time-resolved near-IR luminescence measurements are 0.05 ± 0.01 and 0.06 ± 0.01 in ethanol and in acetonitrile, respectively. The photostability of MBC arises from the 3ππ\* character in the T1 state. The zero-field splitting parameters in the T1 state are D = 0.0901 cm–1 and E = −0.0498 cm–1. The sublevel preferentially populated by intersystem crossing is Ty (y close to in-plane short axis and to the C═O direction).

# A Near-Infrared Neutral pH Fluorescent Probe for Monitoring Minor pH Changes: Imaging in Living HepG2 and HL-7702 Cells\_2009

Kupffer cells (KCs), potent scavenger cells located in hepatic sinusoids, constantly phagocytize and degrade foreign materials to maintain metabolism and clearance. Understanding the strategic KC arrangement which links to their spatial location and function in hepatic lobules, the basic functional unit in the liver, is highly valuable for characterizing liver function. However, selectively labeling KCs and characterizing their function in vivo remains challenging. Herein, a fast self-assembled pomegranate structure-like nanoparticle with “nanopomegranate seeds” of dye aggregates has been developed, which has dual-modality “off/on” capability. This nanopomegranate shows good photostability, a high extinction coefficient, a high KC labeling efficiency (98.8%), and better visualization of KC morphology than commercial FluoSpheres. In vivo photoacoustic (PA) and fluorescence imaging consistently visualize that KCs are strategically distributed along the central vein (CV)–portal triad (PT) axis in each liver lobule: more and larger KCs exist in areas closer to the PTs. The high-resolution PA quantitative data further revealed that the density of KCs was linearly dependent on the rn/rmax ratio (their relative location along the CV–PT axis) (R2 = 0.7513), and the KC density at the outermost layer is almost 246-fold that at the innermost layer (each layer is 8 μm). Notably, the phagocytic ability of KCs located in layers with rn/rmax ratios of 0.167–0.3 varies in a zigzag pattern, as evidenced by their different PA intensities. Additionally, the fluorescence imaging quantitation suggests similar fluorescence activation of nanopomegranate in KCs. Nanopomegranates combined with dual-modality imaging reveal the strategic arrangement of KCs in vivo, greatly extending our understanding of liver physiology.

# Optical and Time-Resolved Electron Paramagnetic Resonance Studies of the Excited States of a UV-B Absorber (4-Methylbenzylidene)camphor\_2013

Improving the photostability of highly luminescent Mn2+ doped all-inorganic halide perovskite nanocrystals (NCs) is challenging because their excellent optical performances are determined by the stable structure and low defect/trap states. The optical properties of Mn2+ doped CsPbCl3 (Mn2+:CsPbCl3) NCs with various Mn2+ doping concentrations under ultraviolet (UV) illumination were studied to unravel their photodegradation by using photoluminescence (PL) spectroscopy at room temperature. The PL intensities of band-edge excitons and Mn2+ ions in the Mn2+:CsPbCl3 NC films significantly decreased due to formation of nonradiative defects/traps in NCs with increasing illumination times. It was surprisingly found that the single- and multiexponential decay times (1.81–1.15 ms) of Mn2+ emissions ranging from 595 to 640 nm observed in the doped NC films with low and high Mn/Pb ratios were almost not varied with increasing UV illumination times. However, the blue-shift of Mn2+ emission was observed in high Mn2+ doping concentration NCs under illumination, which might result from the diffusion of Mn2+ ions to the surface of doped NCs. Further, the surface passivation of Mn2+:CsPbCl3 NCs by using a Cs4PbCl6 shell was found to effectively suppress the photodegradation of Mn2+:CsPbCl3 NCs and enhance the PL stability of Mn2+.

# Self-Assembled “Off/On” Nanopomegranate for In Vivo Photoacoustic and Fluorescence Imaging: Strategic Arrangement of Kupffer Cells in Mouse Hepatic Lobules\_2019

Doubly luminescent core/shell structure nanoparticles were synthesized for biological detection. In the first step gadolinium oxide (Gd2O3) core doped with the luminescent Tb3+ ions was obtained by applying, with modifications, the polyol route, which allows direct precipitation of oxide nanoparticles in a polyalcohol medium. The presence of Tb3+ ions in the Gd2O3 crystalline matrix confers attractive optical properties for long-term studies and multilabeling such as a high photostability and narrow emission bands. The water sensitivity of these particles, which is detrimental for the Tb ion's luminescence, was overcome by embedding the oxide core in a functionalized polysiloxane shell prepared by hydrolysis condensation of a mixture of APTES and TEOS. This protective layer allows the dispersion of the particles in aqueous solution without loss of luminescence intensity. Moreover, the luminescence of polysiloxane-coated Gd2O3 nanoparticles is more intense than that in the case of the naked Gd2O3 core. Due to the presence of amino groups, organic dyes and biotargeting groups (nucleic acid, biotin, streptavidin) were covalently linked to the polysiloxane network. These particles are efficient for detection of biomolecules whose presence is revealed by the high fluorescence of organic dyes and/or the photostable Tb3+ ion's luminescence.

# Ultraviolet Light-Induced Degradation of Luminescence in Mn-Doped CsPbCl3 Nanocrystals\_2019

Phenolic compounds (PCs) such as 4-chlorophenol, 2,4-dichlorophenol, and phenol, can form a surface complex with ZnO. The surface complex was characterized with FTIR, PL, DTG, DRUV−vis, and photoelectrochemical measurement. The surface 4-CP/ZnO complex binds to ZnO through phenolate Zn−O−Ph−Cl linkage, which is much stronger than the phenolate Ti−O−Ph−Cl linkage of the surface 4-CP/TiO2 complex. The formation of the surface complex shifts the absorption response of ZnO from the UV to the visible region through ligand-to-metal charge transfer with excitation of visible photon, and induces efficient visible photocatalytic activity. ZnO exhibits 3.7 times higher photocatalytic activity for the photodegradation of 4-CP than TiO2 under visible irradiation. The much higher visible photocataltyic activity of ZnO than TiO2 is attributed to the higher efficiency of the charge transfer in the former than in the latter evidenced by the much larger photocurrent of PC/ZnO than PC/TiO2. Moreover, the formation of the surface complex results in the substantial improvement of the photostability of ZnO as it leads to a considerable decrease of the surface defect sites of ZnO, and the photogenerated holes trapped on the surface of ZnO probably prefer reacting with the surface complex to reacting with the surface oxygen atom under UV−visible irradiation.

# Nanosized Hybrid Particles with Double Luminescence for Biological Labeling\_2005

Organic semiconductors are of interest for (opto)electronic applications due to their low cost, solution processability, and tunable properties. Recently, natural product-derived organic pigments attracted attention due to their extraordinary environmental stability and unexpectedly good optoelectronic performance, in spite of only partially conjugated molecular structure. Fungi-derived pigments are a naturally sourced, sustainable class of materials that are largely unexplored as organic semiconductor materials. We present a study of the optical and electronic properties of a fungi-derived pigment xylindein, which is secreted by the wood-staining fungi Chlorociboria aeruginosa, and its blends with poly(methyl methacrylate) (PMMA) and crystalline nanocellulose (CNC). Optical absorption spectra of xylindein revealed the presence of two tautomers whose structures and properties were established using density functional theory. Pronounced pigment aggregation in polar solvents and in films, driven by intermolecular hydrogen bonding, was also observed. The pigment exhibited high photostability, electron mobility up to 0.4 cm2/(V s) in amorphous films, and thermally activated charge transport and photoresponse with activation energies of ∼0.3 and 0.2 eV, respectively. The dark and photocurrents in xylindein:PMMA blends were comparable to those in pristine xylindein film, whereas blends with CNC exhibited lower currents due to inhomogeneous distribution of xylindein in the CNC.

# Formation of Surface Complex Leading to Efficient Visible Photocatalytic Activity and Improvement of Photostabilty of ZnO\_2009

Synergistic cancer therapy through the combination of chemotherapy with photothermal therapy has been gained more and more insights. Bimetallic nanostructures with near-infrared (NIR) plasmonic responses are considered prime candidates based on their superior photothermal conversion properties. Herein, novel poly branched Au–Pd bimetallic-nanoflowers-coated betulinic acid liposomes (BA-Lips@Pd@Au NFs) were designed and developed. The as-prepared BA-Lips@Pd@Au NFs with optimal size (144.4 nm) possessed good photostability under NIR-irradiation, high photothermal conversion efficiency (64.6%), and good biocompatibility. Moreover, the hyperthermia of drug delivery induced by NIR-irradiation dramatically improved the cell uptake of nanocapsules and enhanced the chemotherapeutic efficacy of tumor. Upon illumination by NIR light, the BA-Lips@Pd@Au NFs exhibited prominent synergetic effects of chemo-photothermal therapy with a tumor inhibition ratio (91.7%), which was higher than that of chemotherapy or photothermal therapy alone. Therefore, this rational design of nanocapsule with stimuli-responsive capability showed a versatile strategy to provide smart nanocapsule paradigms for cancer therapy.

# Xylindein: Naturally Produced Fungal Compound for Sustainable (Opto)electronics\_2019

Three uncharged push–pull oxazol-5(4H)-ones were synthesized and thoroughly characterized. The examined molecules contained electron-donor and electron-acceptor groups interacting via a π-conjugated bridge. Spectral properties of the oxazol-5(4H)-ones were studied in detail in three solvents of different polarities. The results indicate a solvatochromic shift toward lower energy for the charge-transfer state. The compounds are weakly fluorescent in polar solvents, but they have high fluorescence quantum yields in nonpolar solvents. Their two-photon absorption (2PA) properties were characterized by the open- and closed-aperture Z-scan technique, by the pump–probe technique, and by the two-photon excited fluorescence method. The dyes exhibit relatively high effective two-photon absorption cross sections ranging from 490 to 2600 GM at ∼100 GW/cm2, according to the Z-scan results, which are found, however, to contain significant contribution from higher-order absorption processes. In addition, these compounds display good photostability.

# Self-Assembly of Stimuli-Responsive Au–Pd Bimetallic Nanoflowers Based on Betulinic Acid Liposomes for Synergistic Chemo-Photothermal Cancer Therapy\_2018

Drug molecules bearing multiple charges usually form precipitates with cationic dendrimers, which presents a challenge during the preparation of dendrimer inclusions for these drugs. In the present study, fully acetylated polyamidoamine (PAMAM) dendrimers were proposed as stable vehicles for drug molecules bearing two negative charges such as Congo red and indocyanine green. NMR techniques including 1H NMR and 1H-1H NOESY were used to characterize the host–guest chemistry of acetylated dendrimer and these guest molecules. The cationic PAMAM dendrimer was found to form a precipitate with Congo red and indocyanine green, but the acetylated one avoided the formation of cross-linking structures in aqueous solutions. NOESY studies revealed the encapsulation of Congo red and indocyanine green within the interior cavities of PAMAM dendrimers at mild acidic conditions and acetylated dendrimers show much stronger ability to encapsulate the guest molecules than cationic ones. Also, UV–vis–NIR studies suggest that acetylated dendrimers significantly improve the photostability of indocyanine green and prevent the formation of indocyanine green J-aggregates in aqueous solutions. The present study provides a new insight into dendrimer-based host–guest systems, especially for those guest molecules bearing multiple charges.

# Synthesis and Linear and Nonlinear Optical Properties of Three Push–Pull Oxazol-5(4H)-one Compounds\_2015

Drug molecules bearing multiple charges usually form precipitates with cationic dendrimers, which presents a challenge during the preparation of dendrimer inclusions for these drugs. In the present study, fully acetylated polyamidoamine (PAMAM) dendrimers were proposed as stable vehicles for drug molecules bearing two negative charges such as Congo red and indocyanine green. NMR techniques including 1H NMR and 1H-1H NOESY were used to characterize the host–guest chemistry of acetylated dendrimer and these guest molecules. The cationic PAMAM dendrimer was found to form a precipitate with Congo red and indocyanine green, but the acetylated one avoided the formation of cross-linking structures in aqueous solutions. NOESY studies revealed the encapsulation of Congo red and indocyanine green within the interior cavities of PAMAM dendrimers at mild acidic conditions and acetylated dendrimers show much stronger ability to encapsulate the guest molecules than cationic ones. Also, UV–vis–NIR studies suggest that acetylated dendrimers significantly improve the photostability of indocyanine green and prevent the formation of indocyanine green J-aggregates in aqueous solutions. The present study provides a new insight into dendrimer-based host–guest systems, especially for those guest molecules bearing multiple charges.

# Host–Guest Chemistry of Dendrimer–Drug Complexes: 7. Formation of Stable Inclusions between Acetylated Dendrimers and Drugs Bearing Multiple Charges\_2012

Photothermal therapy (PTT) as a kind of noninvasive tumor treatment has attracted increasing research interest. However, the efficiency of existing PTT agents in the near-infrared (NIR) region is the major problem that has hindered further development of PTT. Herein, we present an effective strategy to construct the efficient photothermal agent by utilizing an intramolecular photoinduced electron transfer (PeT) mechanism, which is able to dramatically improve photothermal conversion efficiency in the NIR region. Specifically, an NIR dye (A1) constructed with dimethylamine moiety as the electron donor and the aza-BODIPY core as the electron acceptor is designed and synthesized, which can be used as a class of imaging-guided PTT agents via intramolecular PeT. After encapsulation with biodegradable polymer DSPE–mPEG5000, nanophotothermal agents with a small size exhibit excellent water solubility, photostability, and long-time retention in tumor. Importantly, such nanoparticles exhibit excellent photothermal conversion efficiency of ∼35.0%, and the PTT effect in vivo still remains very well even with a low dosage of 0.05 mg kg–1 upon 808 nm NIR laser irradiation (0.5 W cm–2). Therefore, this reasonable design via intramolecular PeT offers guidance to construct excellent photothermal agents and subsequently may provide a novel opportunity for future clinical cancer treatment.

# Targeted Nuclear Delivery using Peptide-Coated Quantum Dots\_2011

Quenching and product studies have been performed to demonstrate the suitability of hyperbranched polyethers with a tetrafunctionalized benzophenone core as photocatalysts. The triplet photosensitized transformation of an unsaturated diazo compound has been used as the model reaction. The polymer with highest molecular weight led to a similar product distribution even after several catalytic cycles, which evidences its excellent photostability under prolonged irradiation time. We attribute this to the stabilizing effect of the hyperbranched polymer shell.

# Utilizing Intramolecular Photoinduced Electron Transfer to Enhance Photothermal Tumor Treatment of Aza-BODIPY-Based Near-Infrared Nanoparticles\_2018

Beta amyloid plays a main role in the pathophysiology of Alzheimer’s disease by inducing oxidative stress in the brain. Curcumin, a natural antioxidant, is known to inhibit beta amyloid and beta amyloid induced oxidative stress. However, low bioavailability and photodegradation are the major concerns for the use of curcumin. In the present study, we have formulated apolipoprotein E3 mediated poly(butyl) cyanoacrylate nanoparticles containing curcumin (ApoE3−C-PBCA) to provide photostability and enhanced cell uptake of curcumin by targeting. Prepared nanoparticles were characterized for particle size, zeta potential, entrapment efficiency and in vitro drug release. The entrapment of curcumin inside the nanoparticles was confirmed by X-ray diffraction analysis. Physicochemical characterization confirmed the suitability of the method of preparation. The photostability of curcumin was increased significantly in nanoparticles compared to plain curcumin. In vitro cell culture study showed enhanced therapeutic efficacy of ApoE3−C-PBCA against beta amyloid induced cytotoxicity in SH-SY5Y neuroblastoma cells compared to plain curcumin solution. Beta amyloid is known to induce apoptosis in neuronal cells, therefore antiapoptotic activity of curcumin was studied using flow cytometry assays. From all the experiments, it was found that the activity of curcumin was enhanced with ApoE3−C-PBCA compared to plain curcumin solution suggesting enhanced cell uptake and a sustained drug release effect. The synergistic effect of ApoE3 and curcumin was also studied, since ApoE3 also possesses both antioxidant and antiamyloidogenic activity. It was found that ApoE3 did indeed have activity against beta amyloid induced cytotoxicity along with curcumin. Hence, ApoE3−C-PBCA offers great advantage in the treatment of beta amyloid induced cytotoxicity in Alzheimer’s disease.

# Photocatalysis within Hyperbranched Polyethers with a Benzophenone Core\_2008

Single-chain nanoparticles (SCNPs) are ultrasmall soft nanomaterials constructed via intrachain cross-linking of individual precursor polymer chains, with promising prospects for nanomedicine, catalysis, and sensing, among other different fields. SCNPs are versatile building blocks for the construction of new fluorescent probes with ultrasmall size, higher brightness, and better photostability than previous particle-based systems. Herein, we report on a new, fast, and efficient method to produce SCNPs with intense fluorescence emission in solution which is based on the photoactivation of appropriate aggregation-induced emission (AIE) cross-linking molecules containing azide functional groups. Remarkably, the presence of the azide moiety—that can be transformed to highly reactive nitrene species upon UV irradiation—was found to be essential for the SCNPs to display intense fluorescence emission. We attribute the fluorescence properties of the SCNPs to the immobilization of the initially nonfluorescent AIE molecules via intrachain cross-linking upon photoactivation. Such cross-linking-induced immobilization process activates the AIE mechanism and, hence, leads to fluorescent SCNPs in both solution and solid state.

# ApoE3 Mediated Poly(butyl) Cyanoacrylate Nanoparticles Containing Curcumin: Study of Enhanced Activity of Curcumin against Beta Amyloid Induced Cytotoxicity Using In Vitro Cell Culture Model\_2010

Over the past few years, significant efforts have been made to create new fluorescent probes operating at longer wavelengths, particularly in the second near-infrared (NIR-II) window from 1000 to 1700 nm, offering enhanced tissue penetration compared to light in the visible and first near-infrared window (700–900 nm). However, most of the reported NIR-II fluorophores meet such dilemmas; they are excreted slowly and largely retained within the reticuloendothelial system. Here, we report a rapidly excreted NIR-II lanthanide complex Nd-DOTA (over 50% excreted through the kidneys within 3 h postinjection) with a molecular mass only 0.54 kDa. The NIR-II imaging quality of Nd-DOTA was far superior to that of clinically approved ICG with good photostability and deep tissue penetration (7 mm). Superior tumor-to-normal tissue ratio was successfully achieved to facilitate the abdominal ovarian metastases surgical delineation. Metastases with ≤1 mm can be completely excised under NIR-II bioimaging guidance. Significantly, since the Nd-DOTA structure is same to the clinically approved magnetic resonance imaging (MRI) contrast Gd-DOTA, it will speed up the clinical translation for this novel kind of NIR-II probes in the future.

# Photoactivation of Aggregation-Induced Emission Molecules for Fast and Efficient Synthesis of Highly Fluorescent Single-Chain Nanoparticles\_2018

Neonicotinoids are the newest of the five major classes of insecticides (the others are chlorinated hydrocarbons, organophosphorus compounds, methylcarbamates, and pyrethroids), and they make up approximately one-fourth of the world insecticide market. Nithiazine was the lead compound from Shell Development Co. in California later optimized by Shinzo Kagabu of Nihon Tokushu Noyaku Seizo to increase the potency and photostability, resulting in imidacloprid and thiacloprid. These discoveries are the basis for the International Award for Research in Agrochemicals of the American Chemical Society presented in 2010 to Professor Shinzo Kagabu. Five other neonicotinoids were added by others for the current set of seven commercial compounds. This symposium considers the progress in discovery and development of novel chemotype nicotinic insecticides with enhanced effectiveness, unique biological properties, and maximal safety. Chemorational approaches considered include physicochemical properties, metabolic activation and detoxification, and chemical and structural biology aspects potentially facilitating receptor structure-guided insecticide design.

# Small-Molecule Lanthanide Complexes Probe for Second Near-Infrared Window Bioimaging\_2018

Given the wavelength dependence of tissue transparency and the requirement for sufficiently low background autofluorescence, the development of fluorescent dyes with excitation and emission maxima beyond 700 nm is highly desired, but it is a challenging task. Herein, a new class of fluorescent dyes, named sulfone-rhodamines (SO2Rs), was developed on the basis of the one-atom replacement of the rhodamine 10-position O atom by a sulfone group. Such a modification makes their absorption and emission maxima surprisingly reach up to 700–710 and 728–752 nm, respectively, much longer than their O-, C-, and Si-rhodamine analogs, due to the unusual d\*−π\* conjugation. Among these dyes, SO2R4 and SO2R5, bearing disubstituted meso-phenyl groups, show the greatest potentials for bioimaging applications in view of their wide pH range of application, high photostability, and big extinction coefficients and fluorescence quantum yields. They could quickly penetrate cells to give stable NIR fluorescence, even after continuous irradiation by a semiconductor laser, making them suitable candidates for time-lapse and long-term bioimaging applications. Moreover, they could specifically localize in lysosomes independent of alkylmorpholine targeted group, thus avoiding the problematic alkalization effect suffered by most LysoTrackers. Further imaging assays of frozen slices of rat kidney reveal that their tissue imaging depth is suprior to the widely used NIR labeling agent Cy5.5.

# Neonicotinoid Insecticides: Highlights of a Symposium on Strategic Molecular Designs\_2010

Orthorhombic Nb2O5 nanocrystalline films functionalized with [Ru(bpy)2(4,4′-(PO3H2)2bpy)]2+ were used as the photoanode in dye-sensitized photoelectrosynthesis cells (DSPEC) for hydrogen generation. A set of experiments to establish key properties—conduction band, trap state distribution, interfacial electron transfer dynamics, and DSPEC efficiency—were undertaken to develop a general protocol for future semiconductor evaluation and for comparison with other wide-band-gap semiconductors. We have found that, for a T-phase orthorhombic Nb2O5 nanocrystalline film, the conduction band potential is slightly positive (<0.1 eV), relative to that for anatase TiO2. Anatase TiO2 has a wide distribution of trap states including deep trap and band-tail trap states. Orthorhombic Nb2O5 is dominated by shallow band-tail trap states. Trap state distributions, conduction band energies, and interfacial barriers appear to contribute to a slower back electron transfer rate, lower injection yield on the nanosecond time scale, and a lower open-circuit voltage (Voc) for orthorhombic Nb2O5, compared to anatase TiO2. In an operating DSPEC, with the ethylenediaminetetraacetic tetra-anion (EDTA4–) added as a reductive scavenger, H2 quantum yield and photostability measurements show that Nb2O5 is comparable, but not superior, to TiO2.

# Sulfone-Rhodamines: A New Class of Near-Infrared Fluorescent Dyes for Bioimaging\_2016

The long-term performance of dye-sensitized solar and photoelectrochemical cells is strongly dependent on the stability of surface-bound chromophores and chromophore–catalyst assemblies at metal oxide interfaces. We report here electropolymerization as a strategy for increasing interfacial stability and as a simple synthetic route for preparing spatially controlled, multicomponent films at an interface. We demonstrate that [Fe(v-tpy)2]2+ (v-tpy = 4′-vinyl-2,2′:6′,2″-terpyridine) can be reductively electropolymerized on nanocrystalline TiO2 functionalized with a phosphonate-derivatized Ru(II) polypyridyl chromophore. The outer:inner Fe:Ru ratio can be controlled by the number of reductive electrochemical scan cycles as shown by UV–visible absorption and energy dispersive X-ray spectroscopy measurements. Overlayer electropolymerization results in up to 30-fold enhancements in photostability compared to the surface-bound dye alone. Transient absorbance measurements have been used to demonstrate that photoexcitation and electron injection by the MLCT excited state(s) of the surface-bound RuII complex is followed by directional, outside-to-inside, FeII → RuIII electron transfer. This strategy is appealing in opening a new approach for synthesizing surface-stabilized chromophore–catalyst assemblies on nanocrystalline metal oxide films.

# A Sensitized Nb2O5 Photoanode for Hydrogen Production in a Dye-Sensitized Photoelectrosynthesis Cell\_2012

Topical treatment using photodynamic therapy (PDT) for many types of skin cancers has largely been limited by the inability of existing photosensitizers to penetrate into the deep skin tissue. To overcome these problems, we developed a mesoporous nanovehicle with dual loading of photosensitizers and clinically relevant drugs for combination therapy, while utilizing microneedle technology to facilitate their penetration into deep skin tissue. Sub-50 nm photodynamically active mesoporous organosilica nanoparticles were synthesized with photosensitizers covalently bonded to the silica matrix, which dramatically increased the quantum yield and photostability of these photosensitizers. The mesopores of the nanoparticles were further loaded with small-molecule inhibitors, i.e., dabrafenib and trametinib, that target the hyperactive mitogen-activated protein kinase (MAPK) pathway for melanoma treatment. As-prepared empty nanovehicle was cytocompatible with normal skin cells in the dark, while NIR-irradiated drug-loaded nanovehicle showed a synergistic killing effect on skin cancer cells mainly through reactive oxygen species and caspase-activated apoptosis. The nanovehicle could significantly inhibit the proliferation of tumor cells in a 3D spheroid model in vitro. Porcine skin fluorescence imaging demonstrated that microneedles could facilitate the penetration of nanovehicle across the epidermis layer of skin to reach deep-seated melanoma sites. Tumor regression studies in a xenografted melanoma mouse model confirmed superior therapeutic efficacy of the nanovehicle through combinational PDT and targeted therapy.

# Stabilization of a Ruthenium(II) Polypyridyl Dye on Nanocrystalline TiO2 by an Electropolymerized Overlayer\_2013

ZnxBi2S3+x sensitized platelike WO3 photoelectrodes on FTO substrates were for the first time prepared via a sequential ionic layer adsorption reaction (SILAR) process. The samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet visible spectrometry (UV–vis), and Raman spectra. The results show that the ZnxBi2S3+x quantum dots (QDs) are uniformly coated on the entire surface of WO3 plates, forming a WO3/ZnxBi2S3+x core/shell structure. The ZnxBi2S3+x/WO3 films show a superior ability to capture visible light. High-efficiency photoelectrochemical (PEC) hydrogen generation is demonstrated using the prepared electrodes as photoanodes in a typical three-electrode electrochemical cell. Compared to the Bi2S3/WO3 photoelectrodes, the ZnxBi2S3+x/WO3 photoelectrodes exhibit good photostability and excellent PEC activity, and the photocurrent density is up to 7.0 mA cm–2 at −0.1 V versus Ag/AgCl under visible light illumination. Investigation of the electron transport properties of the photoelectrodes shows that the introduction of ZnS enhances the photoelectrons’ transport rate in the photoelectrode. The high PEC activity demonstrates the potential of the ZnxBi2S3+x/WO3 film as an efficient photoelectrode for hydrogen generation.

# Microneedle-Assisted Topical Delivery of Photodynamically Active Mesoporous Formulation for Combination Therapy of Deep-Seated Melanoma\_2018

New red-emitting conjugated polymers have been successfully synthesized by incorporating classical two-photon absorption (TPA) units, electron-rich units, and a small amount of electron-deficient units along the polymer backbones. Water-dispersible nanoparticles (NPs) based on these polymers were also fabricated for applications in two-photon excitation fluorescence imaging of cell membrane. Through optimization of the polymer/matrix mass ratio and the initial feed concentration of the polymer solution, a high quantum yield (QY) of 24% was achieved for the red-emitting NPs in water. TPA cross section and two-photon action cross section values of these polymers at 750 nm reached up to 1000 GM and 190 GM per repeat unit in aqueous media, 2.5 × 105 GM and 4.7 × 104 GM per NP, respectively. Furthermore, these NPs displayed excellent photostability and biocompatibility. Their applications as two-photon excitation fluorescence probes for cell membrane imaging have been demonstrated in three different cell lines with excellent imaging contrast. These results demonstrated that these polymer NPs hold great potentials as excellent two-photon excitation fluorescence probes in various biological applications.

# Highly Efficient Photoelectrochemical Hydrogen Generation Using ZnxBi2S3+x Sensitized Platelike WO3 Photoelectrodes\_2015

β-Lactoglobulin (β-LG), the major whey protein in the milk of ruminants, has a high affinity for a wide range of compounds. Resveratrol (3,5,4′-trihydroxystilbene), a natural polyphenolic compound found in grapes and red wine, exhibits many physiological effects associated with health benefits. In this study, the interaction of resveratrol with β-LG was investigated using circular dichroism, fluorescence and UV–vis absorbance. Self-association of resveratrol possibly occurs at high concentrations. Resveratrol interacts with β-LG to form 1:1 complexes. Resveratrol is bound to the surface of the protein because β-LG-bound polyphenol is in a weaker hydrophobic environment relative to 75% ethanol. The binding constant for the resveratrol−β-LG interaction is between 104 and 106 M−1, as determined by protein or polyphenol fluorescence. The β-LG−resveratrol interaction may compete with self-association of both the polyphenol and the protein. It has no apparent influence on β-LG secondary structure but partially disrupts tertiary structure. Complexing with β-LG provides a slight increase in the photostability of resveratrol and a significant increase in its hydrosolubility.

# Red-Emitting DPSB-Based Conjugated Polymer Nanoparticles with High Two-Photon Brightness for Cell Membrane Imaging\_2015

Halide perovskites are an extremely promising material platform for solar cells and photonic devices. The role of surface carrier recombination—well known to detrimentally affect the performance of devices—is still not well understood for thin samples where the thickness is comparable to or less than the carrier diffusion length. Here, using time-resolved microspectroscopy along with modeling, we investigate charge-carrier recombination dynamics in halide perovskite CH3NH3PbI3 nanoplatelets with thicknesses from ∼20 to 200 nm, ranging from much lesser than to comparable to the carrier diffusion length. We show that surface recombination plays a stronger role in thin perovskite nanoplatelets, significantly decreasing photoluminescence (PL) efficiency, PL decay lifetime, and photostability. Interestingly, we find that both thick and thin nanoplatelets exhibit a similar increase in PL efficiency with increasing excitation fluence, well described by our excitation saturation model. We also find that the excited carrier distribution along the depth impacts the surface recombination. Using the diffusion–surface recombination model, we determine the surface recombination velocity. This work provides a comprehensive understanding of the role of surface recombination and charge-carrier dynamics in thin perovskite platelets and reveals valuable insights useful for applications in photovoltaics and photonics.

# Interaction of β-Lactoglobulin with Resveratrol and its Biological Implications\_2007

A hydrothermal approach is developed to fabricate Cu2O film via in situ redox reaction between Cu2+ and Cu plate. The crystallization process under different conditions was demonstrated, and the crystal structure of Cu2O was verified by XRD, Raman and XPS characterizations. Simply tuning the anionic groups of Cu2+ can generate different morphologies including rod-like arrays, cross-linked and truncated octahedrals. Mott–Schottky plots and PL spectra indicate that the rod-like arrays possess more copper vacancies than the other two morphologies. In photodegradation, the rod arrays exhibit much better performance, following by truncated and then cross-linked octahedrals. The photostability of the three morphologies was also determined. Although different surface reconstructions occur for the films owing to different charge transfer and consumption pathway, their photoactivities are all enhanced after the first run. Then rod arrays and cross-linked octahedrals show very stable activity, but truncated octahedrals show a gradually decreased activity. This work may be helpful for rationally modulating Cu2O-based materials and understanding their deactive mechanism in photocatalysis.

# Role of Surface Recombination in Halide Perovskite Nanoplatelets\_2018

Diagnostics of Alzheimer’s disease (AD) commonly employ the use of fluorescent thioflavin derivatives having affinity for the amyloid-β (Aβ) proteins associated with AD progression. However, thioflavin probes have limitations in their diagnostic capabilities arising from a number of undesireable qualities, including poor photostability, weak emission intensity, and high emission overlap with the backgound tissue autofluorescence. To overcome such limitations, we have developed nanoformulated probes consisting of a red-emitting fluorescent quantum dot (QD) core encapsulated in a PEGylated shell with benzotriazole (BTA) targeting molecules on the surface (QD-PEG-BTA). The combination of strong red fluorescence, multivalent binding, and decreased backgound signal and nonspecific binding provided the ability of the QD-PEG-BTA probes to achieve detection sensitivites 4 orders of magnitude greater than those of conventional thioflavin derivatives. This study opens the door for the use of QDs in AD detection applications.

# Cu2O Film via Hydrothermal Redox Approach: Morphology and Photocatalytic Performance\_2013

A new substitution pattern of BF2 azadipyrromethene (azaBODIPY) dyes was obtained by phenanthrene fusion through a key palladium-catalyzed intramolecular C–H activation reaction. These [a]-phenanthrene-fused azaBODIPYs have a near planar structure of the phenanthrene-fused azadipyrromethene core in the crystalline state. The chromophore absorbs (log ε > 5) and fluoresces (ϕ = 0.32–0.38) strongly above 700 nm with excellent photostability and may be used as an attractive bright NIR bioimaging agent.

# Enhanced Detection Specificity and Sensitivity of Alzheimer’s Disease Using Amyloid-β-Targeted Quantum Dots\_2016

Oxybenzone (OB) and ferulic acid (FA) both find use in commercial sunscreens; caffeic acid (CA) differs from FA by virtue of an −OH group in place of a −OCH3 group on the aromatic ring. We report the results of ab initio calculations designed to explore the excited state nonradiative relaxation pathways that provide photostability to these molecules and the photoprotection they offer toward UV-A and UV-B radiation. In the case of OB, internal conversion (IC) is deduced to occur on ultrafast time scales, via a barrierless electron-driven H atom transfer pathway from the S1(11nπ\*) state to a conical intersection (CI) with the ground (S0) state potential energy surface (PES). The situation with respect to CA and FA is somewhat less clear-cut, with low energy CIs identified by linking excited states to the S0 state following photoexcitation and subsequent evolution along (i) a ring centered out-of-plane deformation coordinate, (ii) the E/Z isomerism coordinate and, in the case of CA, (iii) an O–H stretch coordinate. Analogy with catechol suggests that the last of these processes (if active) would lead to radical formation (and thus potential phototoxicity), encouraging a suggestion that FA might be superior to CA as a sunscreen ingredient.

# [a]-Phenanthrene-Fused BF2 Azadipyrromethene (AzaBODIPY) Dyes as Bright Near-Infrared Fluorophores\_2017

Near-infrared (NIR)-absorbing organic nanoparticles (ONPs) are emerging candidates for “one-for-all” theranostic nanomaterials with considerations of safety and formulation in mind. However, facile fabrication methods and improvements in the photothermal conversion efficiency (PCE) and photostability are likely needed before a clinically viable set of candidates emerges. Herein, a new organic compound, [porphyrin–diketopyrrolopyrrole (Por–DPP)] with the donor–acceptor structure was synthesized, where porphyrin was used as a donor unit while diketopyrrolopyrrole was used as an acceptor unit. Por–DPP exhibited efficient absorption extending from visible to NIR regions. After self-assembling into nanoparticles (NPs) (∼120 nm), the absorption spectrum of Por–DPP NPs broadened and red-shifted to some extent, relative to that of organic molecules. Furthermore, the architecture of NPs enhanced the acceptor–donor structure, leading to emission quenching and facilitating nonradiative thermal generation. The PCE of Por–DPP NPs was measured and calculated to be 62.5%, higher than most of ONPs. Under 808 nm laser irradiation, the Por–DPP NPs possessed a distinct photothermal therapy (PTT) effect in vitro and can damage cancer cells efficiently in vivo without significant side effects after phototherapy. Thus, the small-molecule porphyrin-based ONPs with high PCE demonstrated promising application in photoacoustic imaging-guided PTT.

# Ab Initio Study of Potential Ultrafast Internal Conversion Routes in Oxybenzone, Caffeic Acid, and Ferulic Acid: Implications for Sunscreens\_2014

Worldwide research efforts have been devoted to organic photovoltaics in the hope of a large-scale commercial application in the near future. To meet the industrial production requirements, organic photovoltaics that can reach power conversion efficiency (PCE) of over 10% along with promising operational device stability are of utmost interest. In the study, we take PCE11:PCBM as a model system, which can achieve over 11% PCE when processed from nonhalogen solvents, to deeply investigate the morphology–performance–stability correlation. We demonstrate that four batches of PCE11 with varying crystalline properties can achieve similar high performance in combination with PCBM. Careful device optimization is necessary in each case to properly address the requirements for the quite distinct microstructures. The bulk-heterojunction (BHJ) microstructure is comprehensively investigated as a function of the macromolecular weight and crystallinity. It is demonstrated that small differences in morphology significantly affect the kinetics and thermodynamic equilibrium of the BHJ microstructure as well as the photostability and thermal stability of the PCE11:PCBM solar cells.

# Small-Molecule Porphyrin-Based Organic Nanoparticles with Remarkable Photothermal Conversion Efficiency for in Vivo Photoacoustic Imaging and Photothermal Therapy\_2019

Electrochemical studies of thiol-capped CdTe nanocrystals in aqueous solution have demonstrated several distinct oxidation and reduction peaks in the voltammograms, with the peak positions being dependent on the size of the nanocrystals. While the size dependence of the reduction and one of the oxidation potentials can be attributed to altering the energetic band positions owing to the quantum size effect, an extraordinary behavior was found for the oxidation peak observed at less positive potentials. In contrast to a prediction based on the quantum size effect, this peak moves to more negative potentials as the nanocrystals' size decreases. Moreover, the contribution of the charge associated with this peak compared to the total charge passed during the nanocrystal oxidation correlates well with the photoluminescence (PL) efficiency of individual fractions of the CdTe nanocrystals. These experimental observations allow a peak to be assigned to the oxidation of Te-related surface traps. The intra-band-gap energy level assigned to these Te-related trap states shifts toward the top of the valence band as the nanocrystal size increases, thus allowing the higher photostability of the larger nanocrystals to be explained. At a certain nanocrystal size, the trap level can even move out of the band gap.

# Comprehensive Investigation and Analysis of Bulk-Heterojunction Microstructure of High-Performance PCE11:PCBM Solar Cells\_2019

The recently reported metalation/transmetalation route for the synthesis of CCC-bis(NHC) pincer ligand supported transition-metal complexes was extended to Pt. 2-(1,3-Bis(N-butylimidazol-2-ylidene)phenylene)(chloro)platinum(II) (1) and its bromo analogue 2 were synthesized and characterized. X-ray crystal structure determinations revealed complexes 1 and 2 to have distorted-square-planar configurations around the metal. Photophysical and thermal properties of these complexes are reported, and their extended photostability in air is discussed and contrasted. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) computations of the ground state and various low-lying excited states have revealed admixing of Pt 5d orbitals and the ligand π\* orbitals for both the ground state and the low-lying excited states of complex 1, indicating the low-lying states to be a mixture of metal-to-ligand charge-transfer and ligand-centered transition (MLCT-LC). Somewhat surprisingly, the computed gas-phase geometry of the excited state of complex 1 had a significant distortion, mostly about the Caryl–Pt–Cl angle. These complexes were congeners of materials for organic light emitting diodes (OLEDs).

# Size-Dependent Electrochemical Behavior of Thiol-Capped CdTe Nanocrystals in Aqueous Solution\_2005

Pairs of noble metal nanoparticles can be used to measure distances via the distance dependence of their plasmon coupling. These “plasmon rulers” offer exceptional photostability and brightness; however, the advantages and limitations of this approach remain to be explored. Here we report detailed plasmon peak versus separation calibration curves for 42- and 87-nm-diameter particle pairs, determine their measurement errors, and describe experimental procedures to improve their performance in biology, nanotechnology, and materials sciences.

# Synthesis, Air Stability, Photobleaching, and DFT Modeling of Blue Light Emitting Platinum CCC-N-Heterocyclic Carbene Pincer Complexes\_2012

Conjugated polymers have attracted significant interest in the bioimaging field due to their excellent optical properties and biocompatibility. Tailor-made poly(p-phenylenevinylene) (PPV) conjugated polymer nanoparticles (NPs) are in here described. Two different nanoparticle systems using poly[2-methoxy-5-(3′,7′-dimethoxyoctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and a functional statistical copolymer 2-(5′-methoxycarbonylpentyloxy)-5-methoxy-1,4-phenylenevinylene (CPM-MDMO-PPV), containing ester groups on the alkoxy side chains, were synthesized by combining miniemulsion and solvent evaporation processes. The hydrolysis of ester groups into carboxylic acid groups on the CPM-MDMO-PPV NPs surface allows for biomolecule conjugation. The NPs exhibited excellent optical properties with a high fluorescent brightness and photostability. The NPs were in vitro tested as potential fluorescent nanoprobes for studying cell populations within the central nervous system. The cell studies demonstrated biocompatibility and surface charge dependent cellular uptake of the NPs. This study highlights that PPV-derivative based particles are a promising bioimaging probe and can cater potential applications in the field of nanomedicine.

# Calibration of Dynamic Molecular Rulers Based on Plasmon Coupling between Gold Nanoparticles\_2005

Tin(IV) porphyrin scaffolds having long-chain (C8 and C16) alkoxyphenyl group at one meso position were synthesized with axial dichloro and dihydroxo ligands. Modifications with respect to the alkoxy chain length and the axial ligands were investigated using UV–vis and fluorescence spectroscopy as well as cyclic voltammetry. Significantly higher molar absorption coefficients were noted with dichloro axial ligands whereas higher fluorescence quantum yields were observed for C8 alkoxy chain substituents. Electrochemical redox data revealed that the porphyrin ring became difficult to reduce consequent to the presence of electron donating alkoxy chain. Evaluation of the aggregation behavior in different organic solvents and DMF-water mixture has been carried out. The singlet oxygen production and photostability data are supportive of their suitability for antibacterial photodynamic therapy. The antibacterial studies carried out in Gram negative (E. coli) and Gram positive (B. subtilis) bacteria using agar well diffusion and LB broth assay revealed selective toxicity in B. Subtilis cells. Fluorescence microscopy and competitive DNA binding studies with Hoechst 33342 revealed DNA binding at the minor groove which was further substantiated with molecular docking studies.

# PPV-Based Conjugated Polymer Nanoparticles as a Versatile Bioimaging Probe: A Closer Look at the Inherent Optical Properties and Nanoparticle–Cell Interactions\_2016

Photoluminescent carbon dots (CDs) have received ever-increasing attention in the application of optical bioimaging because of their low toxicity, tunable fluorescent properties, and ultracompact size. We report for the first time on enhanced photoluminescence (PL) performance influenced by structure effects among the various types of nitrogen doped (N-doped) PL CDs. These CDs were facilely synthesized from condensation carbonization of linear polyethylenic amine (PEA) analogues and citric acid (CA) of different ratios. Detailed structural and property studies demonstrated that either the structures or the molar ratio of PEAs altered the PL properties of the CDs. The content of conjugated π-domains with C═N in the carbon backbone was correlated with their PL Quantum Yield (QY) (up to 69%). The hybridization between the surface/molecule state and the carbon backbone synergistically affected the chemical/physical properties. Also, long-chain polyethylenic amine (PEA) molecule-doped CDs exhibit increasing photostability, but at the expense of PL efficiency, proving that the PL emission of high QY CDs arise not only from the sp2/sp3 carbon core and surface passivation of CDs, but also from the molecular fluorophores integrated in the CDs. In vitro and in vivo bioimaging of these N-doped CDs showed strong photoluminescence signals. Good biocompatibility demonstrates their potential feasibility for bioimaging applications. In addition, the overall size profile of the as-prepared CDs is comparable to the average size of capillary pores in normal living tissues (∼5 nm). Our study provides valuable insights into the effects of the PEA doping ratios on photoluminescence efficiency, biocompatibility, cellular uptake, and optical bioimaging of CDs.

# DNA Targeting Long-Chain Alkoxy Appended Tin(IV) Porphyrin Scaffolds: Photophysical and Antimicrobial PDT Investigations\_2018

Radical cations of polycyclic aromatic hydrocarbons have been postulated to be molecular carriers of diffuse spectroscopic features observed in the interstellar medium. Several important observations made by stellar and laboratory spectroscopists motivated us to undertake a detailed theoretical study attempting to validate the recorded data. In continuation of our work on this subject, we here focus on a detailed theoretical study of the doublet ground (X̃) and low-lying excited (Ã, B̃, and C̃) electronic states of the radical cation of phenanthrene, pyrene, and acenaphthene molecule. A multistate and multimode theoretical model in a diabatic electronic basis is developed here through extensive ab initio quantum chemistry calculations. Employing this model, first-principles nuclear dynamics calculations are carried out to unravel the spectral assignment, time-dependent dynamics, and photostability of the mentioned electronic states of the radical cations. The theoretical results compare well with the observed experimental data.

# High Performance Photoluminescent Carbon Dots for In Vitro and In Vivo Bioimaging: Effect of Nitrogen Doping Ratios\_2015

As the weakly acidic organelle, lysosomes maintain acidic pH ranging from 4.5 to 5.5 and abnormal lysosomal pH levels can result in functional deficiency of lysosomes. To track the pH changes in lysosomes will help us to understand lysosome-related biological processes and diseases. However, pH stimuli-responsive polymer based lysosomal pH fluorescent probe with good water-solubility and biocompatibility have rarely been reported. In this work, based on naphthalimide chromophore and poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA), we designed lysosome-targeted fluorescent probe NapBr-PDM or NapMl-PDM with single or dual responsive sites for monitoring pH changes in lysosomes. Both NapBr-PDM and NapMl-PDM exhibited narrow polydispersity index (PDI), excellent fluorescence properties, water-solubility and high photostability. The synthesized probe NapBr-PDM, with single responsive site, showed fast response to pH changes and well stained lysosomes, which could monitor lysosomal pH changes in cells after incubation with chloroquine. NapMl-PDM had good lysosomes-targeting property and highly sensitive response to pH, which could track lysosomal pH changes. Moreover, NapMl-PDM achieved tracking lysosomal pH changes in cells during lysosomal storage disorder induced by high concentration sucrose solution for the first time. Therefore, this work provided useful tools for monitoring intracellular pH changes as well as studying the relationship between lysosomal pH and its related diseases.

# Theoretical Study on Molecules of Interstellar Interest. II. Radical Cation of Compact Polycyclic Aromatic Hydrocarbons\_2015

LaFeO3 is a p-type oxide that has an ideal bandgap and band edge positions for overall solar water splitting. This study reports an electrochemical synthesis method to produce LaFeO3 as a high surface area, nanoporous photocathode. The resulting electrode generated a photocurrent density of −0.1 mA/cm2 at a potential as positive as 0.73 V vs RHE for photoelectrochemical oxygen reduction with a photocurrent onset potential very close to its flatband potential of 1.45 V vs RHE. Furthermore, without a protection layer, it showed stable photocurrent generation with no sign of photocorrosion. Due to the poor catalytic nature of the LaFeO3 surface for water reduction, the photocurrent obtained for water reduction was not substantial. However, its photostability and its ability to achieve a photovoltage for water reduction greater than 1.2 V encourage further studies on doping to enhance electron–hole separation as well as interfacing appropriate hydrogen evolution catalysts.

# Single/dual responsive pH fluorescent probes based on the hybridization of unconventional fluorescence and fluorophore for imaging lysosomal pH changes in HeLa cells\_2019

Development of “smart” noninvasive bioimaging probes for trapping specific enzyme activities is highly desirable for cancer therapy in vivo. Given that β-galactosidase (β-gal) is an important biomarker for cell senescence and primary ovarian cancers, we design an enzyme-activatable ratiometric near-infrared (NIR) probe (DCM-βgal) for the real-time fluorescent quantification and trapping of β-gal activity in vivo and in situ. DCM-βgal manifests significantly ratiometric and turn-on NIR fluorescent signals simultaneously in response to β-gal concentration, which makes it favorable for monitoring dynamic β-gal activity in vivo with self-calibration in fluorescent mode. We exemplify DCM-βgal for the ratiometric tracking of endogenously overexpressed β-gal distribution in living 293T cells via the lacZ gene transfection method and OVCAR-3 cells, and further realize real-time in vivo bioimaging of β-gal activity in colorectal tumor-bearing nude mice. Advantages of our system include light-up ratiometric NIR fluorescence with large Stokes shift, high photostability, and pH independency under the physiological range, allowing for the in vivo real-time evaluation of β-gal activity at the tumor site with high-resolution three-dimensional bioimaging for the first time. Our work provides a potential tool for in vivo real-time tracking enzyme activity in preclinical applications.

# Photoelectrochemical Properties and Stability of Nanoporous p-Type LaFeO3 Photoelectrodes Prepared by Electrodeposition\_2017

A poly(ethylene glycol) (PEG)-based matrix for studies of affinity interactions is developed and demonstrated. The PEG matrix, less than 0.1 μm thick, is graft copolymerized onto a cycloolefin polymer from a mixture of PEG methacrylates using a free radical reaction initiated by UV light at 254 nm. The grafting process is monitored in real time, and characteristics such as thickness, homogeneity, relative composition, photostability, and performance in terms of protein resistance in complex biofluids and sensor qualities are investigated with null ellipsometry, infrared spectroscopy, and surface plasmon resonance. The matrix is subsequently modified to contain carboxyl groups, thereby making it possible to immobilize ligands in a controlled and functional manner. Human serum albumin and fibrinogen are immobilized and successfully detected by antibody recognition using surface plasmon resonance. The results are encouraging and suggest that the PEG matrix is suitable for biochip and biosensor applications in demanding biofluids.

# Real-Time Tracking and In Vivo Visualization of β-Galactosidase Activity in Colorectal Tumor with a Ratiometric Near-Infrared Fluorescent Probe\_2016

We report the effect of Y2O3 passivation by atomic layer deposition (ALD) using various oxidants, such as H2O, O2 plasma, and O3, on In–Ga–Zn–O thin-film transistors (IGZO TFTs). A large negative shift in the threshold voltage (Vth) was observed in the case of the TFT subjected to the H2O-ALD Y2O3 process; this shift was caused by a donor effect of negatively charged chemisorbed H2O molecules. In addition, degradation of the IGZO TFT device performance after the O2 plasma-ALD Y2O3 process (field-effect mobility (μ) = 8.7 cm2/(V·s), subthreshold swing (SS) = 0.77 V/dec, and Vth = 3.7 V) was observed, which was attributed to plasma damage on the IGZO surface adversely affecting the stability of the TFT under light illumination. In contrast, the O3-ALD Y2O3 process led to enhanced device stability under light illumination (ΔVth = −1 V after 3 h of illumination) by passivating the subgap defect states in the IGZO surface region. In addition, TFTs with a thicker IGZO film (55 nm, which was the optimum thickness under the current investigation) showed more stable device performance than TFTs with a thinner IGZO film (30 nm) (ΔVth = −0.4 V after 3 h of light illumination) by triggering the recombination of holes diffusing from the IGZO surface to the insulator–channel interface. Therefore, we envisioned that the O3-ALD Y2O3 passivation layer suggested in this paper can improve the photostability of TFTs under light illumination.

# Photografted Poly(ethylene glycol) Matrix for Affinity Interaction Studies\_2006

Conjugated polymers possess excellent qualities as fluorescent probes for biomedical applications, because of their extremely high brightness, extinction coefficients, and photostability. Encapsulating these hydrophobic polymers in nanoparticulate form allows transfer to aqueous environments and construction of high-performance fluorescent nanoparticle constructs, and several surface capping strategies have been demonstrated to date. Here, we describe the development of a new class of multifunctional capping ligands for conjugated polymer nanoparticles based on custom-designed amphiphilic peptides. These versatile peptide ligands provide a protective hydrophilic capping layer, chemical handles for further conjugation, and directed biological activity tuned by altering the specific amino acid sequence. We show that (i) cellular uptake can be regulated as a function of peptide composition, and (ii) the nanoparticles show no signs of toxicity under the conditions used, which is a vital health and environmental issue when developing these technologies for clinical use. Finally, we demonstrate that this one-pot method can be applied can be applied to three classes of conjugated polymers and demonstrate potential for multicolor imaging.

# Enhanced Light Stability of InGaZnO Thin-Film Transistors by Atomic-Layer-Deposited Y2O3 with Ozone\_2017

The photocatalytic activities of CdS nanoparticles immobilized in porous regenerated cellulose (RC) films with different pore sizes were investigated. The resulting CdS/RC nanocomposite films were characterized by using transmission electron microscopy, scanning electron microscopy, X-ray diffraction, thermal gravimetric analysis, and UV−vis diffuse reflectance spectroscopy. The mean pore sizes of the porous RC films can be modulated from about 20 to 57 nm by adjusting the concentration of the cellulose solution, and the porous structures within RC film act as reacting sites to lead to the embedment of CdS nanoparticles with a mean particle diameter of about 8 nm. The photocatalytic H2 evolution efficiencies over the obtained CdS/RC nanocomposite films were investigated by using Na2S−Na2SO3 mixed solution as a sacrificial reagent under visible-light (λ ≥ 420 nm) irradiation. Experimental results indicate that the present nanocomposite films revealed obvious predominance, such as high visible-light photoactivity for H2 production, enduring photostability, and convenient regeneration in comparison with CdS nanoparticles suspension system. This new pathway for the fabrication of portable visible-light-driven photocatalyst is important for the H2 production via “green” processes.

# Tailoring Cellular Uptake of Conjugated Polymer Nanoparticles Using Modular Amphiphilic Peptide Capping Ligands\_2015

Conjugated polymer nanoparticles composed of PFT/PS as a core and PEG-COOH on the surface were prepared by a reprecipitating method. The CPNs diaplay excellet properties such as good photostability, low cytotoxicity, and strong brightness, etc. The average diamater of CPNs is 30 nm with a spherical morphology. To realize specific imaging in different parts of tumor cells, the bare CPNs with the carboxyls on the surface were conjugated with antibody or peptide by a covalent mode. Studies display that CPNs modified with anti-EpCAM can recognize MCF-7 tumor cells and locate on the membrane, while CPNs conjugated with transcriptional activator protein (Tat) specifically locate in the cytoplasm of MCF-7 cells. On the basis of the ability of CPNs for producing reactive oxygen species (ROS) under light irradiation, photodynamic therapy for tumor cells was investigated. Due to the long distance and wide diffusion range, MCF-7 tumor cells with CPNs/anti-EpCAM have no obvious change with or without white light irradiation. However, CPNs/Tat exhibits higher killing ability for MCF-7 cells. Noticeably, multifunctional CPNs linked with anti-EpCAM and Tat simultaneously not only can specifically target MCF-7 tumor cells, but also may inhibit and kill these cells. This work develops a potential application platform for multifunctional CPNs in locating imaging, photodynamic therapy, and other aspects.

# CdS/Regenerated Cellulose Nanocomposite Films for Highly Efficient Photocatalytic H2 Production under Visible Light Irradiation\_2009

Composite fibers of poly(vinyl pyrrolidone) (PVP, Mw ≈ 1 300 000) and europium complex Eu(BA)3(TPPO)2 (BA =1-benzoylacetone; TPPO = triphenylphosphine oxide) with strong photoluminescence were prepared by electrospinning. Their luminescent properties were studied in comparison to that of the pure complex. The results indicate that due to decreased symmetry in the composites the excitation bands are split into two different components, peaking at ∼246 and ∼336 nm, respectively, while the ratio of the electronic dipole 5D0-7F2 transitions to the magnetic dipole 5D0-7F1 ones in the emission spectra becomes a little larger. The room temperature fluorescence lifetime for the 5D0 level becomes shorter due to increased radiative and nonradiative transition rates. The temperature dependence of photoluminescence was investigated under 325-nm excitation. It is interesting to observe that in the composite fiber the total emission intensity of the Eu3+ ions changes little below 150 K, while in the pure complex the intensity decreases monotonically with increasing temperature. In addition, the composite fibers exhibit better photostability exposed to ultraviolet lights. These novel luminescent composite fibers have potential application in nanodevices.

# Biological Functionalization of Conjugated Polymer Nanoparticles for Targeted Imaging and Photodynamic Killing of Tumor Cells\_2016

Conjugated polymers containing alternating donor/acceptor units have strong and sharp absorbance peaks in near-infrared (NIR) region, which could be suitable for photothermal therapy. However, these polymers as photothermal transducers are rarely reported because of their water insolubility, which limits their applications for cancer therapy. Herein, we report the donor–acceptor conjugated polymer PBIBDF-BT with alternating isoindigo derivative (BIBDF) and bithiophene (BT) units as a novel photothermal transducer, which exhibited strong near-infrared (NIR) absorbance due to its low band gap (1.52 eV). To stabilize the conjugated polymer physiological environments, we utilized an amphiphilic copolymer, poly(ethylene glycol)-block-poly(hexyl ethylene phosphate) (mPEG-b-PHEP), to stabilize PBIBDF-BT-based nanoparticles (PBIBDF-BT@NPPPE) through a single emulsion method. The obtained nanoparticles PBIBDF-BT@NPPPE showed great stability in physiological environments and excellent photostability. Moreover, the PBIBDF-BT@NPPPE exhibited high photothermal conversion efficiency, reaching 46.7%, which is relatively high compared with those of commonly used materials for photothermal therapy. Accordingly, in vivo and in vitro experiments demonstrated that PBIBDF-BT@NPPPE exhibits efficient photothermal anticancer efficacy. More importantly, PBIBDF-BT@NPPPE could simultaneously encapsulate other types of therapeutic agents though hydrophobic interactions with the PHEP core and achieve NIR-triggered intracellular drug release and a synergistic combination therapy of thermo-chemotherapy for the treatment of cancer.

# Electrospinning Preparation and Photoluminescence Properties of Rare-Earth Complex/Polymer Composite Fibers\_2007

The photophysics and photochemistry of nucleobases are the factors governing the photostability of DNA and RNA, since they are the UV chromophores in nucleic acids. Because the formation of photoproducts involves structural changes in the excited electronic state, we study here the initial excited-state structural dynamics of 9-methyladenine (9-MeA) by using UV resonance Raman (UVRR) spectroscopy. UV resonance Raman intensities are sensitive to the initial excited-state structural dynamics of molecules. Therefore, information about the initial structural changes in the excited-state of a given molecule can be obtained from its UVRR intensities. The resonance Raman spectra of 9-MeA at wavelengths throughout its 262 nm absorption band were measured, and a self-consistent analysis of the resulting resonance Raman excitation profiles and absorption spectrum was performed using a time-dependent wave packet formalism. We found that the initial structural dynamics of this molecule primarily lie along the N3C4, C4C5, C5C6, C5N7, N7C8, and C8N9 stretching vibrations and CH3 deformation vibrations. These results are discussed in the context of photochemistry and other deactivation processes.

# A Donor–Acceptor Conjugated Polymer with Alternating Isoindigo Derivative and Bithiophene Units for Near-Infrared Modulated Cancer Thermo-Chemotherapy\_2016

Composite fibers of poly(vinyl pyrrolidone) (PVP, Mw ≈ 1 300 000) and europium complex Eu(BA)3(TPPO)2 (BA =1-benzoylacetone; TPPO = triphenylphosphine oxide) with strong photoluminescence were prepared by electrospinning. Their luminescent properties were studied in comparison to that of the pure complex. The results indicate that due to decreased symmetry in the composites the excitation bands are split into two different components, peaking at ∼246 and ∼336 nm, respectively, while the ratio of the electronic dipole 5D0-7F2 transitions to the magnetic dipole 5D0-7F1 ones in the emission spectra becomes a little larger. The room temperature fluorescence lifetime for the 5D0 level becomes shorter due to increased radiative and nonradiative transition rates. The temperature dependence of photoluminescence was investigated under 325-nm excitation. It is interesting to observe that in the composite fiber the total emission intensity of the Eu3+ ions changes little below 150 K, while in the pure complex the intensity decreases monotonically with increasing temperature. In addition, the composite fibers exhibit better photostability exposed to ultraviolet lights. These novel luminescent composite fibers have potential application in nanodevices.

# Near-Infrared-Emitting Squaraine Dyes with High 2PA Cross-Sections for Multiphoton Fluorescence Imaging\_2012

Few-atom gold nanoclusters (AuNCs) have been fabricated and used for various fields owing to their remarkable optical and photophysical features. However, the rational design for the antibody-mediated synthesis of fluorescent AuNCs for direct antigen–antibody reactions remains unexplored. In this work, immunoglobulin G (IgG)-functionalized AuNCs (IgG-AuNCs) were successfully prepared via a facile and fast biomineralization process. The generated IgG-AuNCs can emit intense red fluorescence with a high photoluminescence quantum yield. Besides strong emission, the bioactivity of IgG on the IgG-AuNCs can be retained. Surface plasmon resonance measurements suggested that IgG-AuNCs can bind to goat anti-human IgG with an affinity constant of 6.21 × 10–8 M. A simple detection method was then developed using a dot-blot immunoassay with IgG-AuNCs as fluorescent tags. Experimental results confirmed that the IgG-AuNC-based fluorescent reporters had many advantages such as low nonspecific adsorption and good photostability, offering immense potential for the development of efficient biosensors. This work can be extended to other specific antibodies to produce multifunctional AuNCs and utilized to detect and monitor targeted analytes and biological events of interest.

# Immunoglobulin G-Encapsulated Gold Nanoclusters as Fluorescent Tags for Dot-Blot Immunoassays\_2019

Host–guest encapsulation of electron-rich naphthalene molecules into a weakly emissive porous metal–organic framework based on π-electron-deficient (π-acidic) naphthalene diimide tectons leads to orange-emissive crystals, which can be used to sense strongly basic organic amines in a fast response, high photostability, and tunable sensitivity. Moreover, such host–guest inclusion crystals are also a good photochromic probe for the detection of weakly basic N-methyl-2-pyrrolidone and N,N-dimethylformamide molecules.

# Initial Excited-State Structural Dynamics of 9-Methyladenine from UV Resonance Raman Spectroscopy\_2011

Among the palette of previously described fluorescent organic molecules, coumarins are ideal candidates for developing cellular and molecular imaging tools due to their high cell permeability and minimal perturbation of living systems. However, blue-to-cyan fluorescence emission is usually difficult in in vivo applications due to the inherent toxicity and poor tissue penetration of short visible light wavelengths. Here, we introduce a new family of coumarin-based fluorophores, nicknamed COUPY, with promising photophysical properties, including emission in the far-red/near-infrared (NIR) region, large Stokes shifts, high photostability, and excellent brightness. COUPY fluorophores were efficiently synthesized in only three linear synthetic steps from commercially available precursors, with the N-alkylation of a pyridine moiety being the key step at the end of the synthetic route, as it allows for the tuning of the photophysical properties of the resulting dye. Owing to their low molecular weights, COUPY dyes show excellent cell permeability and accumulate selectively in nucleoli and/or mitochondria of HeLa cells, as their far-red/NIR fluorescence emission is easily detected at a concentration as low as 0.5 μM after an incubation of only 20 min. We anticipate that these coumarin scaffolds will open a way to the development of novel coumarin-based far-red to NIR emitting fluorophores with potential applications for organelle imaging and biomolecule labeling.

# Encapsulating Naphthalene in an Electron-Deficient MOF to Enhance Fluorescence for Organic Amines Sensing\_2016

Highly monodispersed nanoparticles of a trivalent silver polydiguanide complex are synthesized by oxidation of the monovalent silver, followed by stabilization of the oxidized higher-valent metal through complexation with a polydiguanide ligand in a reverse microemulsion at room temperature. The synthesized nanoparticles have excellent photostability and displayed superior antibacterial activity toward Gram-positive and Gram-negative prokaryotes of clinical interest in vitro compared to silver sulfadiazine. These nanoparticles may serve as a new generation antibacterial metallopharmaceutical in wound care.

# Redesigning the Coumarin Scaffold into Small Bright Fluorophores with Far-Red to Near-Infrared Emission and Large Stokes Shifts Useful for Cell Imaging\_2017

A paper by Treussart and co-workers in this issue demonstrates the application of photoluminescent nanodiamonds for intracellular labeling as well as mechanistic cellular uptake studies. Findings from this paper reveal that optimal photoluminescence of nitrogen-vacancy color centers can be attained with photostability and no photoblinking, enabling continuous tracking in the cytoplasm over sustained time scales. In addition to the fluorescent properties of the nanodiamonds, internalization assays reveal a primarily endocytic uptake process. A high degree of nanodiamond (∼46 nm in diameter) and endosome colocalization as well as cytoplasmic presence of smaller nanodiamonds was observed. Several attributes of the nanodiamond particles are elucidated in this and other recent studies, ranging from their stability as imaging agents to their potential as intracellular molecular delivery vehicles. These findings give insight into the use of nanodiamonds as an emerging platform for therapeutic and diagnostic (“theranostic”) nanomedicine, forging new foundations and criteria for continued nanodiamond engineering toward downstream clinical relevance and impact.

# Synthesis of Highly Antibacterial Nanocrystalline Trivalent Silver Polydiguanide\_2009

β-Lactoglobulin (β-LG), the major whey protein in bovine milk, binds to a wide range of compounds. Folic acid (FA) is a synthetic form of the B group vitamin known as folates, which are essential cofactors for a variety of physiological processes. The interaction of β-LG with FA was studied using fluorescence spectroscopy to determine the FA binding constant and mode and the influence of the protein on FA photodegradation. At ≤20 μM FA, which may be the critical self-association concentration, the binding constant and number are 2.0 (±0.6) × 106 M−1 and 1.30 (±0.03) when excited at 280 nm and 4.3 (±2.2) × 105 M−1 and 1.17 (±0.04) at 295 nm, as determined by protein intrinsic fluorescence. FA binds to the surface of β-LG, possibly in the groove between the α-helix and the β-barrel. Fluorescence analysis of the pterin portion of FA shows that complexation with β-LG improves FA photostability. It is suggested that β-LG complexes could be used as an effective carrier of FA in functional foods.

# Beyond the Sparkle: The Impact of Nanodiamonds as Biolabeling and Therapeutic Agents\_2009

Because of their extraordinary brightness and photostability, quantum dots (QDs) have tremendous potential for long-term, particle tracking in heterogeneous systems (e.g., living cells, microfluidic flow). However, one of their major limitations is blinking, an intermittent loss of fluorescence, characteristic of individual and small clusters of QDs, that interrupts particle tracking. Recently, several research groups have reported “nonblinking QDs”. However, blinking is the primary method used to confirm nanoparticle aggregation status in situ, and single or small clusters of nanoparticles with continuous fluorescence emission are difficult to discern from large aggregates. Here, we describe a new class of quantum dot-based composite nanoparticles that solve these two seemingly irreconcilable problems by exhibiting near-continuous, alternating-color fluorescence, which permits aggregation status discrimination by observable color changes even during motion across the focal plane. These materials will greatly enhance particle tracking in cell biology, biophysics, and fluid mechanics.

# β-Lactoglobulin/Folic Acid Complexes: Formation, Characterization, and Biological Implication\_2010

A structurally and compositionally well-defined and spectrally tunable artificial light-harvesting system has been constructed in which multiple organic dyes attached to a three-arm-DNA nanostructure serve as an antenna conjugated to a photosynthetic reaction center isolated from Rhodobacter sphaeroides 2.4.1. The light energy absorbed by the dye molecules is transferred to the reaction center, where charge separation takes place. The average number of DNA three-arm junctions per reaction center was tuned from 0.75 to 2.35. This DNA-templated multichromophore system serves as a modular light-harvesting antenna that is capable of being optimized for its spectral properties, energy transfer efficiency, and photostability, allowing one to adjust both the size and spectrum of the resulting structures. This may serve as a useful test bed for developing nanostructured photonic systems.

# Alternating-Color Quantum Dot Nanocomposites for Particle Tracking\_2011

Fluorescent detection of glutathione (GSH) in the living system has attracted much attention, but current fluorescent probes are usually exposed to the exterior environment, leading to photobleaching and premature leakage and subsequently limiting the sensitivity and photostability. Herein, luminescent metal–organic frameworks [Ru(bpy)32+ encapsulated in UiO-66] coated with manganese dioxide nanosheets [MnO2 NS@Ru(bpy)32+–UiO-66] were prepared by an in situ growth method and further explored to construct a GSH-switched fluorescent sensing platform. Because of the splendid fluorescence quenching ability, special probe leakage blocking role and distinguished recognition of the MnO2 NS, and the improved fluorescence of Ru(bpy)32+ by UiO-66, a low background, highly sensitive and selective detection of GSH with a low limit of detection as 0.28 μM was realized. At the same time, the preparation of MnO2 NS@Ru(bpy)32+–UiO-66 nanocomposites is simple and less toxic, and there was no notable loss of cell survivability after being exposed to MnO2 NS@Ru(bpy)32+–UiO-66 below the concentrations of 120 μg mL–1 for 24 h. Consequently, the results coming from this effort suggest that the new sensing platform will have a great potential in the detection of GSH in living cells.

# A DNA-Directed Light-Harvesting/Reaction Center System\_2014

A new rhodamine-based chemosensor 1 with a six-membered spirocyclic ring has been synthesized, which exhibits excellent pH stability and shows selective “turn-on” fluorescent detection of Cu2+ ions over a series of other metal ions including Cu+ ions. The expansion of spirocycle improves the stability and selectivity of the chemosensors in sensing of metal ions. Till today only few rhodamine structures R1–R5 with thiourea-, hydrazine amide-, or pyrrole-decorated six-membered spirocyclic rings are known that exhibit metal-ion sensing via C–N bond cleavage of the spiro ring. In this context, rhodamine compound that responds to the metal ion through C–C bond cleavage of the six-membered spiro ring is completely unknown. The present example is a first-time report that demonstrates selective sensing of Cu2+ ions through C–C bond cleavage over the conventional existing systems in the literature. The chemosensor 1 is cell permeable and can detect Cu2+ in live cells using confocal microscopy in the biologically relevant pH range with high photostability.

# Intracellular Imaging of Glutathione with MnO2 [email protected](bpy)32+–UiO-66 Nanocomposites\_2019

Supported lipid bilayers have been studied intensively over the past two decades. In this work, we study the diffusion of single gold nanoparticles (GNPs) with diameter of 20 nm attached to GM1 ganglioside or DOPE lipids at different concentrations in supported DOPC bilayers. The indefinite photostability of GNPs combined with the high sensitivity of interferometric scattering microscopy (iSCAT) allows us to achieve 1.9 nm spatial precision at 1 ms temporal resolution, while maintaining long recording times. Our trajectories visualize strong transient confinements within domains as small as 20 nm, and the statistical analysis of the data reveals multiple mobilities and deviations from normal diffusion. We present a detailed analysis of our findings and provide interpretations regarding the effect of the supporting substrate and GM1 clustering. We also comment on the use of high-speed iSCAT for investigating diffusion of lipids, proteins, or viruses in lipid membranes with unprecedented spatial and temporal resolution.

# New Six-Membered pH-Insensitive Rhodamine Spirocycle in Selective Sensing of Cu2+ through C–C Bond Cleavage and Its Application in Cell Imaging\_2017

We present the excited-state potential energy profiles of the biologically relevant 9H-keto-amino tautomer of guanine with respect to the radiationless decay via the out-of-plane deformation of the six-membered ring as well as the dissociation of NH bonds. The CASPT2//CASSCF method is employed for the reaction-path calculations. The reaction path for the out-of-plane deformation in the 1ππ\* state leads in a barrierless way to a conical intersection with the electronic ground state. For the NH dissociation via the 1πσ\* state, the 9H-keto-amino tautomer is shown to have lower energy barriers than the 7H tautomers which we have studied recently. These two radiationless decay mechanisms explain the unexpected missing of the biologically relevant form in the resonant two-photon ionization spectrum of guanine in a supersonic jet. It is suggested that these ultrafast deactivation processes provide the biologically relevant tautomer of guanine with a high degree of photostability.

# Tracking Single Particles on Supported Lipid Membranes: Multimobility Diffusion and Nanoscopic Confinement\_2014

Fluorescent carbon quantum dots (CQDs) are synthesized by laser irradiation of carbon glassy particles suspended in polyethylene glycol 200 by two methods, a batch and a flow jet configuration. The flow jet configuration is carried out by the simple combination of common laboratory objects to construct a home-made passage reactor of continuous flow. Despite the simplicity of the system, the laser energy is better harvested by the carbon microparticles, improving the fabrication efficiency a 15% and enhancing the fluorescence of CQDs by an order of magnitude in comparison with the conventional batch. The flow jet-synthesized CQDs have a mean size of 3 nm and are used for fluorescent imaging of transparent healthy and cancer epithelial human cells. Complete internalization is observed with a short incubation time of 10 min without using any extra additive or processing of the cell culture. The CQDs are well fixed in the organelles of the cell even after its death; hence, this is a simple manner to keep the cell information for prolonged periods of time. Moreover, the integrated photostability of the CQDs internalized in in vitro cells is measured and it remains almost constant during at least 2 h, revealing their outstanding performance as fluorescent labels.

# Nonradiative Decay Mechanisms of the Biologically Relevant Tautomer of Guanine\_2008

Films of liquid crystalline copoly(methacrylate)s with photochromic azobenzene and benzanilide side groups and related terpolymers with additional dye side groups were oriented by the irradiation with linearly polarized visible or, alternatively, UV light. The orientational behaviors of the terpolymers with benzoxazole, stilbene, and anthracene moieties were compared. The irradiation conditions for the photoorientation process were optimized concerning wavelength and dose with respect to the absorption of the dyes and their limited photostability. Caused by the cooperativity of the photoorientation process, the light-induced ordering of the azobenzene group is connected with the alignment of the nonphotochromic co-mesogenic and the dye side groups even below the glass transition temperature. The light-induced orientational order generated in the glassy state was significantly amplified by the subsequent annealing of the irradiated films at temperatures within the mesophase of the co- and terpolymers. Amplification factors up to 30 were found in this series of polymers. The photoinduction process and the subsequent amplification by thermotropic self-organization were investigated in dependence of the polymer composition, the irradiation dose, and the wavelength of the incident light. The required dose or the irradiation time was significantly reduced by the optimization of light-induced and thermal processing, respectively. In this way, dichroic polymer films containing different types of dyes were created.

# Fabrication by Laser Irradiation in a Continuous Flow Jet of Carbon Quantum Dots for Fluorescence Imaging\_2018

RNA-based fluorescent probes are currently limited by their low selectivity toward RNA versus DNA, and low specificity to different RNA structures. Poor membrane permeability is another defect of existing fluorogenic RNA probes for intracellular imaging. In this work, a naphthalimide derivative, probe 1, was developed for the rapid and selective detection of intracellular rRNA (rRNA). Probe 1 exhibited a 32-fold fluorescent enhancement in response to rRNA binding and showed desirable selectivity for rRNA versus DNA and other nucleic acids in phosphate buffer at pH 7.2. Importantly, probe 1 displayed excellent permeability of the nucleolus, could be taken up in 1 min by four different cell lines, and may be the fastest nucleolus dye. The excellent selectivity of probe 1 toward rRNA is attributed to the specific interaction between the complicated 3D structures of rRNA, which was confirmed by quantum calculations using molecular docking simulations. An appropriate lipophilic balance in 1 with the hydrophilic amine group and hydrophobic naphthalimide, as well as its high water solubility, guarantees the high permeability of 1 in cell membranes and nucleolus pores, compared to other analogues (e.g., probes 2–8 in this work). Furthermore, enlarged confocal laser micro images of nucleoli and RNase digestion tests revealed that 1 remained highly selective toward rRNA, even for intracellular imaging. As a live cell probe, 1 also exhibited better photostability than the commercial RNA dye, SYTO RNA select.

# Light-Induced Orientation of Liquid Crystalline Terpolymers Containing Azobenzene and Dye Moieties\_2005

An optical molecular imaging contrast agent that is tailored toward lymphatic mapping techniques implementing near-infrared (NIR) fluorescence image-guided navigation in the planning and surgical treatment of cancers would significantly aid in enabling the real-time visualization of the potential metastatic tumor-draining lymph node(s) for their needed surgical biopsy and/or removal, thereby ensuring unmissed disease to prevent recurrence and improve patient survival rates. Here, the development of the first NIR fluorescent rosol dye (THQ-Rosol) tailored to overcome the limitations arising from the suboptimal properties of the generic molecular fluorescent dyes commonly used for such applications is described. In developing THQ-Rosol, we prepared a progressive series of torsionally restrictive N-substituted non-NIR fluorescent rosol dyes based on density functional theory (DFT) calculations, wherein we discerned high correlations amongst their calculated energetics, modeled N–C3′ torsion angles, and evaluated properties. We leveraged these strong relationships to rationally design THQ-Rosol, wherein DFT calculations inspired an innovative approach and synthetic strategy to afford an uncharged xanthene core-based scaffold/molecular platform with an aptly elevated pKa value alongside NIR fluorescence emission (ca.700–900 nm). THQ-Rosol exhibited 710 nm NIR fluorescence emission, a 160 nm Stokes shift, robust photostability, and an aptly elevated pKa value (5.85) for affording pH-insensitivity and optimal contrast upon designed use. We demonstrated the efficacy of THQ-Rosol for lymphatic mapping with in vitro and in vivo studies, wherein it revealed timely tumor drainage and afforded definitive lymph node visualization upon its administration and accumulation. THQ-Rosol serves as a proof-of-concept for the effective tailoring of an uncharged xanthene core-based scaffold/molecular platform toward a specific imaging application using rational design.

# Ribosomal RNA-Selective Light-Up Fluorescent Probe for Rapidly Imaging the Nucleolus in Live Cells\_2019

The development of ultrastable and highly fluorescent heteroatoms-doped graphene quantum dots (GQDs) for bioimaging remains a challenge due to the fluorescence quenching caused by binding between the heteroatoms-based functional groups of the GQDs and common metal ions in biological systems. Here, we developed a facile hydrothermal method to prepare nitrogen–sulfur doped GQDs (NS-GQDs). The fluorescence signals of the NS-GQDs are highly stable in the existence of different metal ions. Two natural products, aspartic acid and cysteine, were utilized as the carbon precursors and heteroatomic (nitrogen and sulfur) sources. The produced NS-GQDs showed a quantum yield up to 19.3 ± 1.7% with a maximum emission of 480 nm under the excitation of 400 nm. The elemental analysis, including X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FTIR), were performed to characterize the composition and surface groups of NS-GQDs. Additionally, the NS-GQDs not only showed notable photostability, but also thermostability and chemical stability. Moreover, the NS-GQDs demonstrated very low cellular cytotoxicity in vitro. Finally, the NS-GQDs were applied for fluorescence imaging of cells, which also exhibited excellent fluorescent stability even with treatment of copper ions. The results indicated that the developed novel NS-GQDs have a promising potential to be used as ultrastable fluorescent agent in the field of bioimaging and biosensing.

# Near-Infrared Fluorescent Rosol Dye Tailored toward Lymphatic Mapping Applications\_2019

Water-soluble upconversion luminescent (UCL) nanoparticles based on triplet–triplet annihilation (TTA) were successfully prepared by coloading sensitizer (octaethylporphyrin Pd complex) and annihilator (9,10-diphenylanthracene) into silica nanoparticles. The upconversion luminescence quantum yield of the nanoparticles can be as high as 4.5% in aqueous solution. As determined by continuous kinetic scan, the nanoparticles have excellent photostability. Such TTA-based upconversion nanoparticles show low cytotoxicity and were successfully used to label living cells with very high signal-to-noise ratio. UCL imaging with the nanoparticles as probe is capable of completely eliminating background fluorescence from either endogenous fluorophores of biological sample or the colabeled fluorescent probe. In particular, such blue-emissive upconversion nanoparticles were successfully applied in lymph node imaging in vivo of living mouse with excellent signal-to-noise ratio (>25), upon low-power density excitation of continuous-wave 532 laser (8.5 mW cm–2). Such high-contrast and low-power excited bioimaging in vivo with a blue-emissive upconversion nanoparticle as probe may extend the arsenal of currently available luminescent bioimaging in vitro and in vivo.

# Nitrogen–Sulfur-Doped Graphene Quantum Dots with Metal Ion-Resistance for Bioimaging\_2019

We have synthesized core/shell NaGdF4:Nd3+/NaGdF4 nanocrystals with an average size of 15 nm and exceptionally high photoluminescence (PL) quantum yield. When excited at 740 nm, the nanocrystals manifest spectrally distinguished, near-infrared to near-infrared (NIR-to-NIR) downconversion PL peaked at ∼900, ∼1050, and ∼1300 nm. The absolute quantum yield of NIR-to-NIR PL reached 40% for core–shell nanoparticles dispersed in hexane. Time-resolved PL measurements revealed that this high quantum yield was achieved through suppression of nonradiative recombination originating from surface states and cross relaxations between dopants. NaGdF4:Nd3+/NaGdF4 nanocrystals, synthesized in organic media, were further converted to be water-dispersible by eliminating the capping ligand of oleic acid. NIR-to-NIR PL bioimaging was demonstrated both in vitro and in vivo through visualization of the NIR-to-NIR PL at ∼900 nm under incoherent lamp light excitation. The fact that both excitation and the PL of these nanocrystals are in the biological window of optical transparency, combined with their high quantum efficiency, spectral sharpness, and photostability, makes these nanocrystals extremely promising as optical biomaging probes.

# Blue-Emissive Upconversion Nanoparticles for Low-Power-Excited Bioimaging in Vivo\_2012

Color centers in solid state crystals have become a frequently used system for single-photon generation, advancing the development of integrated photonic devices for quantum optics and quantum communication applications. In particular, defects hosted by two-dimensional (2D) hexagonal boron nitride (hBN) are a promising candidate for next-generation single-photon sources, due to its chemical and thermal robustness and high brightness at room temperature. The 2D crystal lattice of hBN allows for a high extraction efficiency and easy integration into photonic circuits. Here we develop plasma etching techniques with subsequent high-temperature annealing to reliably create defects. We show how different fabrication parameters influence the defect formation probability and the emitter brightness. A full optical characterization reveals the higher quality of the created quantum emitters, represented by a narrow spectrum, short excited state lifetime, and high single-photon purity. We also investigated the photostability on short and very long time scales. We utilize a wet chemically assisted transfer process to reliably transfer the single-photon sources onto arbitrary substrates, demonstrating the feasibility for the integration into scalable photonic quantum information processing networks.

# Core/Shell NaGdF4:Nd3+/NaGdF4 Nanocrystals with Efficient Near-Infrared to Near-Infrared Downconversion Photoluminescence for Bioimaging Applications\_2012

Sunlight is an ideal source of energy, and converting sunlight into chemical fuels, mimicking what nature does, has attracted significant attention in the past decade. In terms of solar energy conversion into chemical fuels, solar water splitting for hydrogen production is one of the most attractive renewable energy technologies, and this achievement would satisfy our increasing demand for carbon-neutral sustainable energy. Here, we report corrosion-resistant, nanocomposite photoelectrodes for spontaneous overall solar water splitting, consisting of a CdS quantum dot (QD) modified TiO2 photoanode and a CdSe QD modified NiO photocathode, where cadmium chalcogenide QDs are protected by a ZnS passivation layer and gas evolution cocatalysts. The optimized device exhibited a maximum efficiency of 0.17%, comparable to that of natural photosynthesis with excellent photostability under visible light illumination. Our device shows spontaneous overall water splitting in a nonsacrificial environment under visible light illumination (λ > 400 nm) through mimicking nature’s “Z-scheme” process. The results here also provide a conceptual layout to improve the efficiency of solar-to-fuel conversion, which is solely based on facile, scalable solution-phase techniques.

# Fabrication and Deterministic Transfer of High-Quality Quantum Emitters in Hexagonal Boron Nitride\_2018

Real-time tracking of membrane proteins is essential to gain an in-depth understanding of their dynamics on the cell surface. However, conventional fluorescence imaging with molecular probes like organic dyes and fluorescent proteins often suffers from photobleaching of the fluorophores, thus hindering their use for continuous long-term observations. With the availability of fluorescent nanodiamonds (FNDs), which have superb biocompatibility and excellent photostability, it is now possible to conduct the imaging in both short and long terms with high temporal and spatial resolution. To realize the concept, we have developed a facile method (e.g., one-pot preparation) to produce alkyne-functionalized hyperbranched-polyglycerol-coated FNDs for bioorthogonal labeling of azide-modified membrane proteins and azide-modified antibodies of membrane proteins. The high specificity of this labeling method has allowed us to continuously monitor the movements of the proteins of interest (such as integrin α5) on/in living cells over 2 h. The results open a new horizon for live cell imaging with functional nanoparticles and fluorescence microscopy.

# Stable Quantum Dot Photoelectrolysis Cell for Unassisted Visible Light Solar Water Splitting\_2014

Diphenylacetylenes containing chiral menthyl groups [C6H5C≡C−C6H4OCOCH2OR\* and C6H5C≡C−C6H4CO2R\*, R\* = (1R,2S,5R)-(−)-menthyl] are synthesized and polymerized by WCl6−Ph4Sn catalyst. The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, UV, CD, and PL analyses. All the polymers are thermally stable, losing little of their weights when heated to ≥250 °C. They also enjoy high photostability, suffering no change in the molecular weight when exposed to UV irradiation in air for 24 h. The backbones of the polymers are induced to helically rotate by the chiral pendants, as verified by their large specific optical rotations and strong Cotton effects in the backbone absorption region in the solution and aggregate states. The polymers emit green light of 493 and 520 nm when their solutions and nanoparticle suspensions in poor solvents are photoexcited. UV irradiation of the polymer films in air photooxidizes the exposed regions, generating two-dimensional luminescent photopatterns.

# Bioorthogonal Fluorescent Nanodiamonds for Continuous Long-Term Imaging and Tracking of Membrane Proteins\_2019

Graphdiyne has attracted much interest from researchers for their potential applications in energy storage, catalysis, and biomedical areas. As one of the derivatives of graphdiyne, graphdiyne quantum dots (GDQDs) may possess superior bioactivity due to active acetylene units. However, the biological application of biocompatible GDQDs have not been reported so far. Herein, GDQDs with uniform size and good crystallization were prepared via a classical solvothermal method. The GDQDs exhibit excitation- and pH-dependent fluorescence emission as well as superior photostability, demonstrating their potential for bioimaging. The GDQDs demonstrate efficient cellular uptake and cell imaging without induction of detectable cytotoxic effects in vitro. Systematical safety evaluation further confirmed good biocompatibility of the GDQDs in vivo. Our study preliminarily validates the application of the GDQDs in biomedicine and encourages more thorough studies for better realizing the potential of GDQDs.

# Helical and Luminescent Disubstituted Polyacetylenes: Synthesis, Helicity, and Light Emission of Poly(diphenylacetylene)s Bearing Chiral Menthyl Pendant Groups\_2011

This review describes the growing partnership between super-resolution imaging and plasmonics, by describing the various ways in which the two topics mutually benefit one another to enhance our understanding of the nanoscale world. First, localization-based super-resolution imaging strategies, where molecules are modulated between emissive and nonemissive states and their emission localized, are applied to plasmonic nanoparticle substrates, revealing the hidden shape of the nanoparticles while also mapping local electromagnetic field enhancements and reactivity patterns on their surface. However, these results must be interpreted carefully due to localization errors induced by the interaction between metallic substrates and single fluorophores. Second, plasmonic nanoparticles are explored as image contrast agents for both superlocalization and super-resolution imaging, offering benefits such as high photostability, large signal-to-noise, and distance-dependent spectral features but presenting challenges for localizing individual nanoparticles within a diffraction-limited spot. Finally, the use of plasmon-tailored excitation fields to achieve subdiffraction-limited spatial resolution is discussed, using localized surface plasmons and surface plasmon polaritons to create confined excitation volumes or image magnification to enhance spatial resolution.

# Synthesis and Imaging of Biocompatible Graphdiyne Quantum Dots\_2019

A new strategy has been developed to synthesize conjugated polymer (CP) nanoparticles (CPNs) with numerous surface hydroxyl groups via click chemistry between a CP and hyperbranched polyglycerol (HPG) in miniemulsion. Laser light scattering and TEM characterizations indicate that the synthesized CPNs have spherical shapes with uniform sizes tunable in the range of 40–210 nm simply by adjusting the feed amount of the oil phase or surfactant in the miniemulsion. The obtained CPNs have good water dispersibility and orange emission with high fluorescence quantum yields of 23 ± 2%. Detailed spectroscopy studies reveal that the CPNs have shown stable fluorescence against pH change, ionic strength variation, or protein disturbance. In addition, they have good photostability and low cytotoxicity, which make them an ideal fluorescent moiety for cellular imaging. This study provides important fundamental understanding of cross-linking modification on CP to form CPNs, which will stimulate further research on synthesis and application of advanced CPNs.

# Super-Resolution Imaging and Plasmonics\_2017

The introduction of multiple components into one crystalline metal–organic framework (MOF) provides a feasible approach to fully understand the correlation of component heterogeneity and the whole performance. Herein, photoactive tetratopic chlorin (TCPC) ligands with different geometry and connectivity have been successfully incorporated into the Hf-UiO-66 archetype structure without altering the underlying topology by a facile strategy. Unlike previous porphyrin-nanoscale-MOFs (porphyrin-NMOFs) with homogeneous periodical porphyrin arrangements typically for photodynamic therapy (PDT) usage, we demonstrate that TCPC component heterogeneity within as-synthesized TCPC-UiO possesses both PDT and photothermal therapy (PTT) simultaneously, but PTT takes a more potent antitumor efficacy as proven in several photophysical characterizations and biological experiments in vitro. The high photothermal conversion efficiency, favorable photostability and biocompatibility, and strong X-ray attenuating ability of the Hf element within TCPC-UiO make it a potential platform for further application in multimodal CT/thermal/photoacoustic imaging. Additionally, TCPC-UiO shows an impressive anticancer activity against H22 tumor-bearing mice in vivo, and its tumor inhibition rate is above 90%. We anticipate that the current work may offer in-depth insight into the component heterogeneity and property relationship and also extend biological applications of NMOFs.

# Facile Synthesis of Stable and Water-Dispersible Multihydroxy Conjugated Polymer Nanoparticles with Tunable Size by Dendritic Cross-Linking\_2012

We report the synthesis and characterization of two amine reactive fluorescent dyes with efficient two-photon absorption (2PA) properties and high fluorescence quantum yields. Bioconjugation of these dyes with the DC-101 antibody proved to be useful for selectively imaging the vascular endothelial growth factor receptor 2 (VEGFR-2) in cells expressing this receptor in vitro and in “whole” mounted excised tumors (ex vivo) by two-photon fluorescence microscopy (2PFM). The penetration depths reached within the tumors by 2PFM was over 800 μm. In addition, the concentration of dye required for incubation of these bioconjugates was in the picomolar domain, the probes possessed very good photostability, and the 2PFM setup did not require any additional means of increasing the collection efficiencies of fluorescent photons to achieve the relatively deep tissue imaging that was realized, due, in large part, to the favorable photophysical properties of the new probes.

# Nanoscale Mixed-Component Metal–Organic Frameworks with Photosensitizer Spatial-Arrangement-Dependent Photochemistry for Multimodal-Imaging-Guided Photothermal Therapy\_2018

The photoluminescence (PL) properties of several recently synthesized ligand-stabilized polynuclear gold(I) selenide complexes were investigated. [Au18Se8(dppe)6]Br2 {dppe = bis(diphenylphosphanyl) ethane} (I) is distinguished by the bright-red long-lived PL (phosphorescence) in the solid state, photosensitization of singlet oxygen, 1O2, in solution, and high photostability. The quantum yield of PL, φPL, is (7.5 ± 0.5) × 10-2 for the polycrystalline I at 293 K (determined using an integrating sphere) and increases up to ∼0.8 at 77 K. The quantum yield of 1O2 is 0.17 ± 0.02 in O2-saturated dichloromethane solutions. [Au10Se4(dpppe)4]Br2 {dpppe = bis(diphenylphosphanyl)pentane} (II) shows a broad near-infrared PL at 880 nm in dichloromethane [φPL = (4 ± 1) × 10-3], which is shifted up to ∼1020 nm in the solid II at 77 K (φPL ∼ 3 × 10-3). Although the quantum efficiency of II as a luminophor is quite moderate, it is comparable to that of organic infrared laser dyes such as Styryl-20 and IR26. A particular configuration of the Au10Se4 core appears to be crucial for the near-infrared PL:  the “isomeric” complexes [Au10Se4(dppm)4]Br2 {dppm = bis(diphenylphosphanyl) methane} (III) and [Au10Se4(depe)4]Cl2 {depe = bis(diethylphosphanyl) ethane} (IV) show no significant PL.

# Two-Photon Fluorescence Vascular Bioimaging with New Bioconjugate Probes Selective toward the Vascular Endothelial Growth Factor Receptor 2\_2011

Biomimetic fluorescent nanoprobes capable of emitting near-infrared (NIR) fluorescence (λmax ≈ 720 nm) upon excitation of 800 nm light were developed. The key conjugated polymer enabled two-photon absorption and Förster resonance energy transfer (FRET) processes within the nanoprobes, which imparted the nanoprobes with ideal NIR-incoming-NIR-outgoing fluorescence features. The cancer cell membrane (CM) coating endowed these nanoprobes with perfect biocompatibility and highly specific targeting ability to homologous tumors. It was believed that CM encapsulation provided an additional protecting layer for the photoactive components residing in the core of nanoprobes for retaining their intrinsic fluorescing ability in the physiological milieu. The long-term structural integrity, excellent photostability (fluorescence decrease <10% upon 30 min illumination of 800 nm pulse laser), high NIR fluorescence quantum yield (∼20%), and long in vivo circulation time of the target nanoprobes were also confirmed. The ability of these feature-packed nanoprobes for circumventing the challenges of absorption and light scattering caused by cellular structures and tissues was definitely confirmed via in vivo and in vitro experiments. The superior performances of these nanoprobes in terms of fluorescence signaling as well as targeting specificity were verified in intravital fluorescence imaging on tumor-bearing model mice. Specifically, these nanoprobes unequivocally enabled high-resolution visualization of the fine heterogeneous architectures of intravital tumor tissue, which proclaims the great potential of this type of probe for high-contrast fluorescence detection of thick biological samples in practical applications.

# Novel Photophysical Properties of Gold Selenide Complexes:  Photogeneration of Singlet Oxygen by [Au18Se8(dppe)6]Br2 and Near-Infrared Photoluminescence of [Au10Se4(dpppe)4]Br2\_2002

The crystal-structure-dependent luminescence properties of cadmium selenide quantum dots (QDs) in their cubic zincblende (Zb-CdSe) and hexagonal wurtzite (Wz-CdSe) phases have been investigated by maintaining their optical band gaps as well as the relative ratios of capping ligands the same. The Zb-CdSe QDs exhibited excellent photostability and high photoluminescence quantum yield (ϕL = 0.375) compared with Wz-CdSe QDs (ϕL = 0.046). Detailed X-ray photoelectron spectroscopic (XPS) investigation revealed an important finding that the surface of Zb-CdSe is rich with Cd2+ ions, which leads to the formation of CdO layer. This was further confirmed by analyzing the (i) Cd-to-Se stoichiometric ratio of zincblende QDs (2:1 on surface and 1:1 after sputtering) and (ii) core-level XPS spectra of oxygen. In contrast, the Cd-to-Se stoichiometric ratio was found to be same (1:1) for Wz-CdSe QDs throughout the crystal. Thus, the high luminescence of Zb-CdSe is attributed to the formation of a thin layer of CdO, leading to a type-I core–shell structure, which passivates the surface defects and confines the charge carriers. On the basis of the present investigation it is clear that the crystal structure plays a decisive role in modulating the surface properties of QDs, which determine the luminescence properties.

# Cancer Cell Membrane-Biomimetic Nanoprobes with Two-Photon Excitation and Near-Infrared Emission for Intravital Tumor Fluorescence Imaging\_2018

Nanostructured gold surfaces were prepared over silicon and glass surfaces using evaporation and sputtering techniques, respectively. The surface enhanced Raman scattering (SERS) activity of these surfaces was investigated for dye molecules such as Methylene Blue and Rhodamine 6G using excitation wavelengths of 532 and 632.8 nm. Our results clearly emphasize that the SERS signal strongly depends on the nature of the surface and is further amplified under electronic resonance conditions. In addition, time-dependent spectral collection of the SERS and the surface-enhanced fluorescence (SEF) of Rhodamine 6G signals were obtained and showed similar behavior that could be fitted using a multiexponential model. This suggests a similar photobleaching mechanism for both SERS and SEF signals. We suggest that the study of molecules photostability under enhanced electromagnetic field should be extremely interesting for the further development of optical near-field spectroscopy.

# Luminescence Properties of CdSe Quantum Dots: Role of Crystal Structure and Surface Composition\_2013

Photoredox catalytic activation of organic molecules via single-electron transfer processes has proven to be a mild and efficient synthetic methodology. However, the heavy reliance on expensive ruthenium and iridium complexes limits their applications for scale-up synthesis. To this end, photoactive metal–organic frameworks (MOFs) exhibit unique advantages as novel heterogeneous photocatalytic systems, yet their utilization toward organic transformations has been limited. Here we describe the preparation and synthetic applications of four isostructural porphyrinic MOFs, namely, UNLPF-10a, -10b, -11, and -12, which are composed of free base, InIII-, SnIVCl2-, and SnIV-porphyrin building blocks, respectively. We demonstrate that the metalation with high valent metal cations (InIII and SnIV) significantly modifies the electronic structure of porphyrin macrocycle and provides a highly oxidative photoexcited state that can undergo efficient reductive quenching processes to facilitate organic reactions. In particular, UNLPF-12 exhibits both outstanding photostability and efficient photocatalytic activities toward a range of important organic transformations including aerobic hydroxylation of arylboronic acids, amine coupling, and the Mannich reaction.

# Surface-Enhanced Raman and Fluorescence Spectroscopy of Dye Molecules Deposited on Nanostructured Gold Surfaces\_2010

S,N-Codoped carbon quantum dots (SNCQDs) with a quantum yield (QY) of 23% have been synthesized using lotus root as a carbon source and glutathione (GSH) as a nitrogen and sulfur source. The obtained SNCQDs exhibited many excellent features such as a simple preparation process, high fluorescence QY, satisfactory photostability, superior water solubility, and biocompatibility. The SNCQDs combined with Cu2+ were used as a novel off–on nanoprobe for 6-thioguanine (TG). Initial fluorescence is significantly quenched in this sensing system via electron transfer from SNCQDs to Cu2+. Fluorescence is recovered after adding TG owing to Cu2+–TG complex formation between Cu2+ and TG. A novel off–on fluorescent nanoprobe was presented for highly sensitive determination of TG. Under optimal conditions, the nanoprobe exhibited a wide linearity range of 0.005–80 μmol/L for TG and a detection limit of 1.6 nmol/L. The designed off–on nanoprobe was successfully utilized for detecting TG in plasma and urine of a leukemia patient and imaging of TG in living T24 cells.

# Porphyrin-Metalation-Mediated Tuning of Photoredox Catalytic Properties in Metal–Organic Frameworks\_2015

Two near-infrared luminescent probes with Stokes-shift and single-photon anti-Stokes-shift fluorescence properties for sensitive determination of pH variance in lysosomes have been synthesized. A morpholine residue in probe A, which serves as a targeting group for lysosomes in viable cells, was attached to the fluorophores via a spirolactam moiety, while a mannose residue was ligated to probe B, resulting in an increased biocompatibility and solubility in water. Probes A and B contain closed spirolactam moieties, and show no Stokes-shift or anti-Stokes-shift fluorescence under neutral or alkali conditions. However, the probes incrementally react to pH variance from 7.22 to 2.76 with measurable increases in both Stokes-shift and anti-Stokes-shift fluorescence at 699 and 693 nm under 645 and 800 nm excitation, respectively. This acid-activated fluorescence is produced by the breaking of the probe spirolactam moiety, which greatly increased the overall π-conjugation in the probes. These probes possess upconversion near-infrared fluorescence imaging advantages including minimum cellular photodamage, increased tissue penetration, and minimum biological fluorescence background. They display an excellent photostability with a low dye photobleaching and show a good biocompatibility. They are selective and capable of detecting pH variances in lysosomes at excitation with two different wavelengths, i.e., 645 and 800 nm.

# Facile Syntheses of S,N-Codoped Carbon Quantum Dots and Their Applications to a Novel Off–On Nanoprobe for Detection of 6-Thioguanine and Its Bioimaging\_2019

Continuing progress in the field of organic polymer photovoltaic (PV) devices requires the development of new materials with better charge-transport efficiency. To improve this parameter, we have investigated surface-attached bilayer polymer PV thin films prepared starting from a covalently attached monolayer of an electroactive initiator using sequential electropolymerization of dithiophene and its derivatives. These systems were found to show significantly increased photocurrent generation quantum yields as compared to systems made through conventional approaches. In addition, the described PV thin films possess remarkable mechanical, air, and photostability. These properties likely arise from the more uniform and better ordered bulk layer morphologies as well as tighter covalently bonded contacts at the interfacial junctions, contributing to improved charge transport. While more studies on the fundamental reasons behind the discovered phenomenon are currently underway, this information can be readily applied to build more efficient organic polymer photovoltaics.

# New Near-Infrared Fluorescent Probes with Single-Photon Anti-Stokes-Shift Fluorescence for Sensitive Determination of pH Variances in Lysosomes with a Double-Checked Capability\_2018

Chemotherapeutic drugs frequently encounter multiple drug resistance in the field of cancer therapy. The strategy has been explored with limited success for the ablation of drug-resistant tumor via intravenous administration. In this work, the rationally designed light-triggered nanoparticles with multipronged physicochemical and biological features are developed to overcome cisplatin resistance via the assembly of Pt(IV) prodrug and cyanine dye (Cypate) within the copolymer for efficient ablation of cisplatin-resistant tumor. The micelles exhibit good photostability, sustained release, preferable tumor accumulation, and enhanced cellular uptake with reduced efflux on both A549 cells and resistant A549R cells. Moreover, near-infrared light not only triggers the photothermal effect of the micelles for remarkable photothermal cytotoxicity, but also leads to the intracellular translocation of the micelles and reduction-activable Pt(IV) prodrug into cytoplasm through the lysosomal disruption, as well as the remarkable inhibition on the expression of a drug-efflux transporter, multidrug resistance-associated protein 1 (MRP1) for further reversal of drug resistance of A549R cells. Consequently, the multipronged effects of light-triggered micelles cause synergistic cytotoxicity against both A549 cells and A549R cells, and thus efficient ablation of cisplatin-resistant tumor without regrowth. The multipronged features of light-triggered micelles represent a versatile synergistic approach for the ablation of resistant tumor in the field of cancer therapy.

# Self-Assembled Monolayer Initiated Electropolymerization: A Route to Thin-Film Materials with Enhanced Photovoltaic Performance\_2008

The potential use of polymer light-emitting devices is ultimately limited by their low quantum efficiency as well as by their poor stability against oxygen and moisture. To simultaneously solve these drawbacks, light-emitting devices using the polymer/layered silicate nanocomposite with good gas-barrier properties were fabricated by blending poly[2-methoxy-5-(2‘-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with organoclay. The 2-dimensional nanocomposite film shows higher photoluminescence (PL) output and better photostability when compared with the pure MEH-PPV film of the same thickness. Electroluminescence (EL) efficiency is also enhanced. This 2-dimensional lamellar type nanocomposite structure efficiently confines not only both electrons and holes to enhance the recombination rate but also excitons to improve singlet radiative decay. By analyzing transient EL behavior, it was found that the charge carrier mobility of the nanocomposite device was reduced, which suggests that effective charge blocking improves the bipolar recombination rates. Additionally, the isolation of polymer chains within a confined geometry by intercalation prevents excitons from finding low-energy trap sites. Therefore, PL and EL quantum yield is improved.

# Multipronged Design of Light-Triggered Nanoparticles To Overcome Cisplatin Resistance for Efficient Ablation of Resistant Tumor\_2015

We studied the dependence of single-molecule fluorescence on the size of nearby metal particles. The silver particles were synthesized with average diameters of metal cores being 5, 20, 50, 70, and 100 nm, respectively. A single-stranded oligonucleotide was chemically bound to a single silver particle and a Cy5-labeled complementary single-stranded oligonucleotide was hybridized with the particle-bound oligonucleotide. The space between the fluorophore and metal core was separated by a rigid hybridized DNA duplex of 8 nm length. The single fluorescence images and intensity traces were recorded by scanning confocal microscopy. The single fluorophore-labeled 50 nm silver particles displayed the most enhanced intensity, a factor of 17-fold increase relative to the free fluorophores in the absence of metal. Numerical simulations by the finite-difference time-domain (FDTD) method and results from Mie theory were used to compare with the experimental results. The 50 nm silver particles were also labeled by multiple fluorophores. The fluorescence intensity of multiple fluorophore-labeled metal particles increases dramatically with the loading number and reached 400-fold relative to the free single fluorophore when the loading number of fluorophore per metal particle was 50. The fluorophore also displayed better photostability when binding on the metal particle. These results can aid us to develop novel nanoscale fluorophores for clinical diagnostics and bioassay.

# Efficient Photoluminescence and Electroluminescence from Environmentally Stable Polymer/Clay Nanocomposites\_2001

The efficiency of the energy relaxation processes occurring in hydroxyphenylbenzotriazole polymer photostabilizers following absorption of ultraviolet (UV) radiation has been investigated and found to depend strongly on the stabilizer structure and the nature of the solvent or polymer substrate. Steady-state absorption and fluorescence, and picosecond fluorescence spectroscopy measurements were carried out on a number of these compounds. The very rapid excited-state intramolecular proton transfer (ESIPT) process responsible for the exceptional photostability of these derivatives is influenced by the hydrogen-bonding properties and polarity of the surrounding medium. The ESIPT process is prevented effectively in those molecules in which the intramolecular hydrogen bonding is disrupted by hydroge-bonding or steric interactions with the solvent or polymer environment.

# Single-Molecule Studies on Fluorescently Labeled Silver Particles:  Effects of Particle Size\_2007

Perovskite solar cells hold great promise as prospective alternatives of renewable power sources. Recently hole blocking layer-free perovskite solar cells, getting rid of complex and high-temperature fabrication processes, have engaged in innovative designs of photovoltaic devices. However, the elimination of the hole blocking layer constrains the energy conversion efficiencies of perovskite solar cells and severely degrades the stabilities. In this paper a simple approach (without energy-consuming and time-consuming procedures) for the fabrication of hole blocking layer-free perovskite solar cells has been demonstrated by an integration of copper–silver alloy nanoparticles, which are synthesized by the wet chemical method with controllable diameters and elemental compositions. The rear-side integration of the subwavelength-sized silver–copper alloy particles (200 nm diameter), through a spraying/drying method, realizes a pronounced absorption enhancement of the perovskite layer by effectively light scattering in a broadband wavelength range and achieves a series resistance decrease of the solar cell because of high electrical conductivities of the alloy particles. The particle integration achieves the highest efficiency of 18.89% due to the significant improvement in both optical and electrical properties of solar cells, making this device one of the highest-performing hole blocking layer-free perovskite solar cells and plasmonic perovskite solar cells. Moreover, the copper-based nanoparticles prevent the perovskite from diffusing into metal back electrodes. Because the diffusion can lead to a severe corrosion of the Au electrode and thus an efficiency degradation, the alloy nanoparticle integration between the perovskite and the electrode results in 80% and 200% improvements in the long-term stability and the photostability of solar cells, respectively. Through the proposed simple and effective fabrication process, our results open up new opportunities in the manufacturability of perovskite solar cells.

# Photophysics of Hydroxyphenylbenzotriazole Polymer Photostabilizers\_1989

To convert greenhouse gas CO2 to available energy by using solar energy is a promising approach for addressing energy dilemma and global warming issues. Although CdS as a photocatalyst can achieve CO2 reduction to fuel, there are still two main problems of activity and stability to be solved. Herein, a simple hydrothermal method with the presence of a little quantity of H2O2 is used to prepare CdS with Cd vacancies, which can promote the separation of photogenerated electrons and holes for activity improvement. It is found that the best catalyst 0.4CdS demonstrates not only high CO selectivity over other carbonaceous products, but also a considerable CO production rate of 316 μmol g–1 h–1, which is 2.1 times as high as that of pure CdS for CO2 reduction under visible light irradiation. In addition, an efficient solution through an additional feeble negative voltage to improve the photostability of 0.4CdS is achieved, which makes this sample remain 94.2% of its original CO2 photoelectrocatalytic reduction performance after four cycles. Thus, this study provides a facile strategy to address the stability and activity issues of CdS under visible light irradiation, which is presumably suitable for improving the other semiconductors with low stability and activity for highly efficient CO2 reduction.

# Hole Blocking Layer-Free Perovskite Solar Cells with High Efficiencies and Stabilities by Integrating Subwavelength-Sized Plasmonic Alloy Nanoparticles\_2019

Seven D–A−π–A-based indoline (IND) dyes that were designed via quantitative-structure–property relationship modeling have been comprehensively investigated using computational approaches to evaluate their prospect of application in future dye-sensitized solar cells (DSSCs). An array of optoelectronic properties of the isolated dye and dyes adsorbed on a TiO2 cluster that simulates the semiconductor were explored by density functional theory (DFT) and time-dependent DFT methods. Light absorption spectra, vertical dipole moment, shift of the conduction band of semiconductor, excited state lifetime, driving force of electron injection, photostability of the excited state, and exciton binding energy were computed. Our study showed that the presence of an internal acceptor such as pyrido[3,4-b]pyrazine (pyrazine) would influence greater the open circuit voltage (VOC), compared to the benzothiadiazole moiety. Considering the balance between the VOC and JSC (short circuit current) along with the all calculated characteristics, the IND3, IND5, and IND10 are the most suited among the designed dyes to be used as potential candidates for the photo-efficient DSSCs. The present study provides the results of rational molecular design followed by exploration of photophysical properties to be used as a valuable reference for the synthesis of photo-efficient dyes for DSSCs.

# H2O2 Treated CdS with Enhanced Activity and Improved Stability by a Weak Negative Bias for CO2 Photoelectrocatalytic Reduction\_2019

Monitoring cellular redox homeostasis is critical to the understanding of many physiological functions ranging from immune reactions to metabolism, as well as to the understanding of pathological development ranging from tumorigenesis to aging. Nevertheless, there is currently a lack of appropriate probes for this ambition, which should be reversibly, sensitively, and promptly responsive to a wide range of physiological oxidants and reductants. In this work, a redox-sensitive fluorescence-switchable probe is designed based on graphene quantum dots (GQDs) functionalized with a chelated redox Fe2+/Fe3+ couple. The underlying mechanism is investigated and discussed. The high sensitivity and fast response are attributable to the fact that the GQD’s photoluminescence is highly sensitive to photon-induced electron transfer because of its ultrasmall size and associated prominent quantum confinement effect. Also taking advantages of GQDs’ excellent photostability, biocompatibility, and readiness for cell uptake, our reversibly tunable fluorescence probe is employed to monitor in real time the triggered dynamic change of the intracellular redox state. This addition to the limited arsenal of available redox probes shall be useful to the still poorly understood redox biology, as well as for monitoring environment or chemical processes involving redox reactions.

# Electronic Structure and Optical Properties of Designed Photo-Efficient Indoline-Based Dye-Sensitizers with D–A−π–A Framework\_2019

We achieved two types of laser emissions from aqueous quantum dots (QDs) using the same high-Q-factor optofluidic ring resonator (OFRR) platform. In the first type, 2 μM QDs were in bulk buffer solution that filled the entire OFRR cavity volume. The lasing threshold was 0.1 μJ/mm2, over 3 orders of magnitude lower than the state-of-the-art. In the second type of laser, the QDs were immobilized as a single layer on the interface between the OFRR inner wall and buffer solution with a surface density as low as 3 × 109–1010 cm–2. The lasing threshold of 60 μJ/mm2 was achieved. In both bulk solution and single-layer lasing cases, the laser emission persisted even under 5–10 min of uninterrupted pulsed optical excitation that was well above the corresponding lasing threshold, indicative of high photostability of the QD laser. This was in sharp contrast to organic-dye-based lasers, which underwent quick photobleaching during the laser operation under similar pumping conditions. Theoretical analysis is also carried out to elucidate the advantages of QD-based optofluidic lasers over those based on dyes. Our work opens the door to a plethora of applications where optofluidic QD lasers can replace dye-based optofluidic lasers in biosensing and on-chip miniaturized laser development.

# Monitoring Dynamic Cellular Redox Homeostasis Using Fluorescence-Switchable Graphene Quantum Dots\_2016

Considering the chemistry of the formation and physics at interfaces, we report on the heterostructure of a promising new energy material, Au–Cu2ZnSnS4 (Au-CZTS), and investigate the impact of coupling on Au on improving both the photostability and the photoresponse behavior. We focus primarily on the fundamental issues involved in bringing together two dissimilar materials having different chemical and physical properties in a single building block where one is a multinary semiconductor nanomaterial and the other is a plasmonic noble metal. The formation of heteroepitaxy at the junction of Au and CZTS was investigated for two different phases of CZTS. Considering epitaxy formation along the {111} planes of Au, it was observed that the wurtzite and tetragonal phases of CZTS exhibit coincident site epitaxy with different periodic intervals. A detailed study of this epitaxy formation with Au in both phases of CZTS has been carried out and reported. Because Au-CZTS is a promising new material, we have further investigated its photocurrent and photoresponse behavior and compared them with the properties and behavior of pure CZTS. We believe that these findings will help the energy-materials community, providing guidelines for investigating new functional materials and their applications.

# Optofluidic Lasers with Aqueous Quantum Dots\_2015

Incorporation of photochromic compounds to polymer matrix through chemical bonding results in an enhancement of photoactivity and stabilization of optical properties. Here, spiropyran ethyl acrylate monomer (SPEA) was synthesized, and then photochromic particles bearing epoxy functional groups were prepared through semicontinuous emulsion copolymerization. Dynamic light scattering (DLS) and scanning electron microscopy (SEM) results depicted an increase in particle size and particle size distribution with the increase in SPEA monomer–surfactants ratio. Studies on photochromic properties by UV–vis analysis demonstrated a decrease in the absorption intensity despite the increase in SPEA content due to the enhancement in particle size. The prepared acrylic copolymer particles showed reasonable photostability, photoreversibility, and fast photoresponsivness according to the convenient test methods under UV/vis irradiation. DSC and DMTA analyses indicate an increase in Tg of the obtained copolymers with the increase in SPEA content. Finally, stimuli-responsive cellulosic papers were prepared by impregnation, and their photochromic behavior was investigated in dry and wet forms in various media under UV radiation. Morphology studies, due to stabilization of the photochromic copolymer on cellulose fibers, were conducted by SEM micrographs and showed good adhesion and compatibility between the two phases.

# Coincident Site Epitaxy at the Junction of Au–Cu2ZnSnS4 Heteronanostructures\_2015

Rapidly emerging techniques of super-resolution single-molecule microscopy of living cells rely on the continued development of genetically encoded photoactivatable fluorescent proteins. On the basis of monomeric TagRFP, we have developed a photoactivatable TagRFP protein that is initially dark but becomes red fluorescent after violet light irradiation. Compared to other monomeric dark-to-red photoactivatable proteins including PAmCherry, PATagRFP has substantially higher molecular brightness, better pH stability, substantially less sensitivity to blue light, and better photostability in both ensemble and single-molecule modes. Spectroscopic analysis suggests that PATagRFP photoactivation is a two-step photochemical process involving sequential one-photon absorbance by two distinct chromophore forms. True monomeric behavior, absence of green fluorescence, and single-molecule performance in live cells make PATagRFP an excellent protein tag for two-color imaging techniques, including conventional diffraction-limited photoactivation microscopy, super-resolution photoactivated localization microscopy (PALM), and single particle tracking PALM (sptPALM) of living cells. Two-color sptPALM imaging was demonstrated using several PATagRFP tagged transmembrane proteins together with PAGFP-tagged clathrin light chain. Analysis of the resulting sptPALM images revealed that single-molecule transmembrane proteins, which are internalized into a cell via endocytosis, colocalize in space and time with plasma membrane domains enriched in clathrin light-chain molecules.

# Preparation of Stimuli-Responsive Functionalized Latex Nanoparticles: The Effect of Spiropyran Concentration on Size and Photochromic Properties\_2015

The development of novel photothermal ablation agents as cancer nanotheranostics has received a great deal of attention in recent decades. Biocompatible fucoidan (Fu) is used as the coating material for gold nanorods (AuNRs) and subsequently conjugated with monoclonal antibodies against epidermal growth factor receptor (anti-EGFR) as novel photothermal ablation agents for cancer nanotheranostics because of their excellent biocompatibility, biodegradability, nontoxicity, water solubility, photostability, ease of surface modification, strongly enhanced absorption in near-infrared (NIR) regions, target specificity, minimal invasiveness, fast recovery, and prevention of damage to normal tissues. Anti-EGFR Fu-AuNRs have an average particle size of 96.37 ± 3.73 nm. Under 808 nm NIR laser at 2 W/cm2 for 5 min, the temperature of the solution containing anti-EGFR Fu-AuNRs (30 μg/mL) increased by 52.1 °C. The anti-EGFR Fu-AuNRs exhibited high efficiency for the ablation of MDA-MB-231 cells in vitro. In vivo photothermal ablation exhibited that tumor tissues fully recovered without recurrence and finally were reconstructed with normal tissues by the 808 nm NIR laser irradiation after injection of anti-EGFR Fu-AuNRs. These results suggest that the anti-EGFR Fu-AuNRs would be novel photoablation agents for future cancer nanotheranostics.

# Bright Monomeric Photoactivatable Red Fluorescent Protein for Two-Color Super-Resolution sptPALM of Live Cells\_2010

Semiconducting polymer dots (Pdots) represent a new class of ultrabright fluorescent probes for biological imaging. They exhibit several important characteristics for experimentally demanding in vitro and in vivo fluorescence studies, such as their high brightness, fast emission rate, excellent photostability, nonblinking, and nontoxic feature. However, controlling the surface chemistry and bioconjugation of Pdots has been a challenging problem that prevented their widespread applications in biological studies. Here, we report a facile yet powerful conjugation method that overcomes this challenge. Our strategy for Pdot functionalization is based on entrapping heterogeneous polymer chains into a single dot, driven by hydrophobic interactions during nanoparticle formation. A small amount of amphiphilic polymer bearing functional groups is co-condensed with the majority of semiconducting polymers to modify and functionalize the nanoparticle surface for subsequent covalent conjugation to biomolecules, such as streptavidin and immunoglobulin G (IgG). The Pdot bioconjugates can effectively and specifically label cellular targets, such as cell surface marker in human breast cancer cells, without any detectable nonspecific binding. Single-particle imaging, cellular imaging, and flow cytometry experiments indicate a much higher fluorescence brightness of Pdots compared to those of Alexa dye and quantum dot probes. The successful bioconjugation of these ultrabright nanoparticles presents a novel opportunity to apply versatile semiconducting polymers to various fluorescence measurements in modern biology and biomedicine.

# Anti-EGFR Antibody Conjugation of Fucoidan-Coated Gold Nanorods as Novel Photothermal Ablation Agents for Cancer Therapy\_2017

A small drug molecule, L-DOPA, was converted into well-defined dendritic macromolecules. Their monodisperse nature was shown by NMR, MALDI-TOF-MS, and PAGE. A third-generation L-Dopa dendrimer contained 30 L-Dopa residues, which made up its core, branches, and periphery. Individual L-Dopa moieties in the dendrimer were connected to one another via hydrolyzable diester linkages. These Dopa dendrimers showed a 20-fold increase in aqueous solubility and enhanced photostability in solutions over L-Dopa under identical conditions.

# Bioconjugation of Ultrabright Semiconducting Polymer Dots for Specific Cellular Targeting\_2010

Two molecular assemblies with one Ru(II)-polypyridine photosensitizer covalently linked to one Ru(II)(bda)L2 catalyst (1) (bda = 2,2′-bipyridine-6,6′-dicarboxylate) and two photosensitizers covalently linked to one catalyst (2) have been prepared using a simple C–C bond as the linkage. In the presence of sodium persulfate as a sacrificial electron acceptor, both of them show high activity for catalytic water oxidation driven by visible light, with a turnover number up to 200 for 2. The linked photocatalysts show a lower initial yield for light driven oxygen evolution but a much better photostability compared to the three component system with separate sensitizer, catalyst and acceptor, leading to a much greater turnover number. Photocatalytic experiments and time-resolved spectroscopy were carried out to probe the mechanism of this catalysis. The linked catalyst in its Ru(II) state rapidly quenches the sensitizer, predominantly by energy transfer. However, a higher stability under photocatalytic condition is shown for the linked sensitizer compared to the three component system, which is attributed to kinetic stabilization by rapid photosensitizer regeneration. Strategies for employment of the sensitizer-catalyst molecules in more efficient photocatalytic systems are discussed.

# Synthesis and Characterization of Water-Soluble and Photostable L-DOPA Dendrimers\_2006

Two Pd(II) complexes based on tetradentate chelate ligands with either a 1,2,4-triazolyl (Pd1) or 1,2,3-triazolyl (Pd2) unit were synthesized, and their structure–property relationships were studied. Both Pd1 and Pd2 are rare bright deep blue Pd(II) phosphors with contrasting properties. Pd1 displays stimuli-responsive luminescence in response to UV irradiation, concentration, or temperature change, which is ascribed to the facile switching of monomer to excimer emission. In contrast, a similar stimuli-responsive luminescence was not observed for Pd2. Crystal structures and time-dependent density functional theory computational studies established that the excimer formation of Pd1 is caused by electronically favored intermolecular π–π interactions and less steric protection of the Pd core because of the position of its alkyl chains, compared to Pd2. In solution, the excimer emission of Pd1 shows a much greater sensitivity toward oxygen than the monomer emission with a very large Stern–Volmer constant (Ksv) that is more than twice that of the monomer emission. Both Pd(II) complexes are found to be outstanding oxygen sensors in ethyl cellulose films with superior sensitivity (Ksvapp = 0.228–0.346 Torr–1) over their Pt(II) equivalents (Ksvapp = 0.00674–0.0110 Torr–1), owing to their long phosphorescence decay lifetimes. Furthermore, Pd1 shows an excellent photostability, compared to the Pt(II) analogue, making it one of the best and highly robust oxygen sensors based on cyclometalated metal complexes.

# Sensitizer-Catalyst Assemblies for Water Oxidation\_2015

Organic semiconductors have attracted considerable attention due to their applications in low-cost (opto)electronic devices. Many successful organic materials utilize blends of several types of molecules that contribute different functions (e.g., serving as donors and acceptors in solar cells). In blends, the local environment, which is inherently heterogeneous, strongly influences the (opto)electronic performance and photostability. We use functionalized fluorinated pentacene (F8 TCHS-Pn) molecules as single-molecule probes of the nanoscale environment in blends containing donor and acceptor molecules incorporated into a polymer (PMMA) matrix. Single F8 TCHS-Pn donor (D) molecules were imaged in PMMA in the presence of functionalized indenofluorene (TIPS-IF) or PCBM acceptor (A) molecules using wide-field fluorescence microscopy at various concentrations. Long-lived dark states attributed to a reversible formation of an endoperoxide (TCHS-EPO) were observed, and the EPO formation and reversal processes, which evolved upon acceptor addition, were quantified. Our study provides a nanoscale-level insight into how the presence of acceptor molecules alters the photophysics of the donor molecules dispersed in the polymer. Kinetics of the F8 TCHS-Pn photo-oxidation reaction and its reversal in such blends are determined by a fine balance of the acceptor-modified morphology (which in our case speeds up the photo-oxidation and slows down its reversal) and singlet oxygen quenching by acceptors (which prevents repeated photo-oxidation/reversal events).

# Multiresponsive Tetradentate Phosphorescent Metal Complexes as Highly Sensitive and Robust Luminescent Oxygen Sensors: Pd(II) Versus Pt(II) and 1,2,3-Triazolyl Versus 1,2,4-Triazolyl\_2019

D–A−π–A dyes differ from the traditional D−π–A framework having several merits in dye-sensitized solar cell (DSSC) applications. With regard to D−π–A dyes, D–A−π–A dyes red-shift absorption spectra and show particular photostability. Nevertheless, the effects of internal acceptor on the charge transfer (CT) probability are unclear. We employed density functional theory (DFT), time-dependent DFT (TD-DFT), and TD-DFT molecular dynamics (MD) simulations to investigate the effects of internal acceptor on the photophysical properties of D–A−π–A dyes on DSSCs. Our calculations show the absorption bands of D–A−π–A dyes with strong electron-withdrawing internal acceptors exhibiting significant characteristics of dual CT; the excited electron density is transferred to the internal and terminal acceptors simultaneously. Particularly, the internal acceptor traps a significant amount of electron density upon photoexcitation. The TD-DFT MD simulations at 300 K show that only a small amount of excited electron density is pushing and pulling between the internal acceptor and terminal acceptor moieties; the thermal energy is not high enough to drive the electron density from the internal acceptor to the terminal acceptor. Our study reveals the nature of CT bands of D–A−π–A dyes providing a theoretical basis for further rational engineering.

# Single-Molecule Level Insight into Nanoscale Environment-Dependent Photophysics in Blends\_2017

Covalent attachment of solvent-sensitive fluorescent dyes to proteins is a powerful tool for studying protein conformational changes, ligand binding, or posttranslational modifications. We report here new merocyanine dyes that make possible the quantitation of such protein activities in individual living cells. The quantum yield of the new dyes is sharply dependent on solvent polarity or viscosity, enabling them to report changes in their protein environment. This is combined with other stringent requirements needed in a live cell imaging dye, including appropriate photophysical properties (excitation >590 nm, high fluorescence quantum yield, high extinction coefficient), good photostability, minimal aggregation in water, and excellent water solubility. The dyes were derivatized with iodoacetamide and succinimidyl ester side chains for site-selective covalent attachment to proteins. A novel biosensor of Cdc42 activation made with one of the new dyes showed a 3-fold increase in fluorescence intensity in response to GTP-binding by Cdc42. The dyes reported here should be useful in the preparation of live cell biosensors for a diverse range of protein activities.

# Effects of Internal Electron-Withdrawing Moieties in D–A−π–A Organic Sensitizers on Photophysical Properties for DSSCs: A Computational Study\_2018

The accurate and sensitive monitoring and imaging of mitochondrial pH in living cells play vital roles in chemical biology and biomedicine. Herein, we design a novel ratiometric fluorescent chemical probe for monitoring and imaging the pH of mitochondria in living cells based on congo-red (CR)-modified dual-emission semiconducting polymer dots (Pdots) via a competitive fluorescence resonance energy transfer (FRET) mechanism. The Pdots are synthesized by triphenylphosphonium (TPP)-modified polyoxyethylene nonylphenylether (CO-520), poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), poly(9,9-dioctylfluorene)-co-(4,7-di-2-thienyl-2,1,3-benzothiadiazole) (PF-DBT5), and poly(styrene-co-maleic anhydride) (PSMA) via a nanoprecipitation method, and the prepared Pdots are further chemically linked with pH-sensitive, nonfluorescent CR to obtain the mitochondria-targeted pH fluorescent probes. This Pdots-based probe consists of two luminescent components including PFO and PF-DBT5 as fluorescence donors, an acid–base indicator CR as an energy acceptor, and TPP as the mitochondria-targeting group. At a different pH region, the FRET efficiency between CR and PFO or CR and PF-DBT5 can be modulated. This probe exhibits good biocompatibility, a wide pH detection range from 2.57 to 8.96, good reversibility, high selectivity, and excellent photostability for pH monitoring. This probe allows for the detecting and imaging of mitochondrial pH in living cells with satisfactory results.

# Solvent-Sensitive Dyes to Report Protein Conformational Changes in Living Cells\_2003

Herein, we report the modulation of ZnO for enhancement of its ability toward plasmonic absorption of near-infrared (NIR) photons through coupling of graphene (GR). The reported modification led GR–ZnO to be a promising photocatalyst by the complete removal of poisonous and nonvolatile potassium cyanide from water. The photocatalytic degradation of cyanide was revealed by exposing it to NIR laser and comparing with the rate of UV, visible, and sunlight using their apparent reaction rate constants derived from the Langmuir–Hinshelwood model. The heteronanostructured GR–ZnO promoted rapid photo-oxidation of cyanide under illumination with NIR laser rather than UV, visible, and sunlight. It was assessed that the photothermal effect (PTE) is the main cause for higher catalytic efficiency of GR–ZnO in the presence of NIR radiations. Except for the NIR radiations, GR–ZnO does not show any indication of PTE by irradiating with UV, visible, or sunlight. On account of its significance, the PTE of GR–ZnO in KCN solution was evaluated and compared with its individual components viz., GR and ZnO upon exposure to a 980 nm laser system. Furthermore, it has been revealed that the PTE of GR–ZnO was proportional to its concentration. In addition to its effectiveness in the degradation of cyanide, GR–ZnO retained its special structure and exhibited an outstanding photostability after its repeated use in three successive cycles.

# A Mitochondria-Targeted Ratiometric Biosensor for pH Monitoring and Imaging in Living Cells with Congo-Red-Functionalized Dual-Emission Semiconducting Polymer Dots\_2017

Bi2O2CO3/BiOI composites were fabricated at room temperature for the first time by a facile method. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–vis diffuse reflectance spectra (UV–vis DRS), and nitrogen adsorption–desorption techniques were employed to characterize the physiochemical properties of the composites. The photocatalytic activities of Bi2O2CO3, BiOI, and Bi2O2CO3/BiOI were evaluated through the photocleaning of wastewater which contained rhodamine-B, methylene blue, crystal violet, or a mixture of them under visible-light irradiation (λ ≥ 420 nm). The photocatalytic activity of Bi2O2CO3/BiOI is much higher than that of its components. Moreover, the composite shows good photostability and recyclability. The excellent catalytic efficiency of the Bi2O2CO3/BiOI composite is deduced closely related to Bi2O2CO3/BiOI heterojunctions whose presence is generally regarded to be a favorable factor for the separation of photogenerated electrons and holes. Moreover, ·OH was found to be the main active species for the photocatalytic interactions. The catalyst shows potential application in the treatment of dye-containing wastewater.

# Graphene-Coupled ZnO: A Robust NIR-Induced Catalyst for Rapid Photo-Oxidation of Cyanide\_2017

Precise patterning and localization of functional nanomaterials is the key step for miniaturization and building of optoelectronic devices. Present study utilizes a robust methodology for the multicolor patterning of luminescent Indium Phosphide/Zinc Sulfide Quantum Dot (InP/ZnS QD) film, by taking the advantage of QD’s enhanced photostability over organic dyes. The photoirradiation regulates the composition of donor–acceptor pair, and thereby, the efficiency of Förster Resonance Energy Transfer (EFRET) in QD–dye nanohybrid film. The photopatterned films are reusable over multiple cycles without any compromise of the color clarity, owing to the reversible switching between FRET ON and OFF states. The highlight of the present work is the use of a single QD nanohybrid system to create multicolor luminescent patterns; as opposed to the common practice of using different-colored QDs. FRET assisted photopatterning of luminescent InP/ZnS QD films provides a fundamentally unique and cost-effective approach for the manufacturing of luminescent optoelectronic devices.

# Förster Resonance Energy Transfer Regulated Multicolor Photopatterning from Single Quantum Dot Nanohybrid Films\_2019

Synthesis of highly luminescent carbon dots (CDs) from waste materials gains much attention in the current scenario. We have converted waste expanded polystyrene (EPS), a nonbiodegradable environmental pollutant, into multifunctionalized fluorescent CDs. This can be a good scaling up approach for the large-scale synthesis of nitrogen-doped CDs with a high photoluminescence (PL) quantum yield (QY) of ∼20%. The as prepared CDs exhibit excellent water solubility and a longer PL lifetime (in nanoseconds). They also possess excellent photostability, low cytotoxicity, and stable luminescence QY in different solution environments. Selective and sensitive detection of Au3+ ions is demonstrated using these CDs as fluorescence probes, and a LOD of 53 nM is achieved. A detailed investigation revealed that the observed PL quenching is due to “coordination-induced aggregation caused PL quenching” mechanism.

# Bi2O2CO3/BiOI Photocatalysts with Heterojunctions Highly Efficient for Visible-Light Treatment of Dye-Containing Wastewater\_2012

The discovery of new two-dimensional (2D) perovskite halides has created sensation recently because of their structural diversity and intriguing optical properties. The toxicity of Pb-based perovskite halides led to the development of Pb-free halides. Herein, we have demonstrated a one-pot solution-based synthesis of 2D ultrathin (∼1.78 nm) few-layer (2–4 layers) nanoplates (300–600 nm lateral dimension), nanosheets (0.6–1.5 μm), and nanocrystals of layered Cs3Bi2I9 by varying the reaction temperature from 110 to 180 °C. We have established a mechanistic pathway for the variation of morphology of Cs3Bi2I9 with temperature in the presence of organic capping ligands. Further, we have synthesized the bulk powder of Cs3Bi2I9 by mechanochemical synthesis and liquid-assisted grinding and crystalline ingot by vacuum-sealed tube melting. 2D nanoplates and bulk Cs3Bi2I9 demonstrate optical absorption edge along with excitonic transition. Photoluminescence properties of individual nanoplates were studied by super-resolution fluorescence imaging, which indicated the blinking behavior down to the level of an individual Cs3Bi2I9 nanoplate along with its emission at the far-red region and high photostability.

# Green Synthesis of Multifunctionalized, Nitrogen-Doped, Highly Fluorescent Carbon Dots from Waste Expanded Polystyrene and Its Application in the Fluorimetric Detection of Au3+ Ions in Aqueous Media\_2017

Clinical diagnostics and therapeutics of tumors are significantly benefitted by the development of multifunctional theranostic agents, which integrate tumor targeting, imaging, and therapeutics. However, the integration of imaging and therapy functionalities to a unimolecular framework remains a great challenge. Herein, a family of amphiphilic gemini iridium(III) complexes (GIC), Ir1–Ir6, are synthesized and characterized. The presence of quaternary ammonium (QA) groups endows GIC with adjustable water solubility and excellent self-assembly properties. Spectroscopic and computational results reveal that introducing QA groups into cyclometalating ligands (ĈN ligands) can overcome the drawback of aggregation-caused emission quenching and ensure Ir1–Ir3 with high emission intensity and excellent singlet oxygen (1O2) generation ability in aqueous media. Cell-based assays indicate that Ir3 shows higher cellular uptake efficiency and localizes specifically in the mitochondria, as well as exhibits outstanding photostability and an impressive phototoxicity index with satisfactory performance in mitochondria-targeted imaging and photodynamic therapy (PDT) of tumor cells. Furthermore, in vivo studies further prove that Ir3 possesses excellent antitumor activity and remarkably inhibits the growth of the HepG2 cells under PDT treatment. Consequently, this study presents a promising strategy for designing clinical application potential multifunctional iridium complex theranostic agents for mitochondria-targeted imaging and PDT in a single molecular framework.

# Synthesis of Ultrathin Few-Layer 2D Nanoplates of Halide Perovskite Cs3Bi2I9 and Single-Nanoplate Super-Resolved Fluorescence Microscopy\_2018

Absorption of ultraviolet radiation by DNA bases results in ultrafast internal conversion to the ground state, which minimizes photodamage. However, exogenous and endogenous alkylating agents present in the cellular environment can methylate the nucleobases in DNA. In particular, methylation of guanosine at the O6 position in DNA leads to the formation of the O6-methylguanosine adduct, which may alter the photostability of DNA. This contribution demonstrates that O6-methylation of guanosine red shifts its ground-state absorption spectrum and slows down the rate of internal conversion to the ground state by ∼40-fold in aqueous solution. The 40-fold decrease in the rate of excited-state decay increases the probability of photodamage within cellular DNA. It is proposed that the longer decay lifetime corresponds to relaxation of the excited-state population in O6-methylguanosine along a C6-puckered reaction coordinate in the 1ππ\*(La) potential energy surface that runs parallel to an ultrafast internal conversion pathway along a C2-puckered coordinate.

# Amphiphilic Gemini Iridium(III) Complex as a Mitochondria-Targeted Theranostic Agent for Tumor Imaging and Photodynamic Therapy\_2019

In recent years, strenuous efforts have been devoted to exploring ZnO functionalized TiO2 nanotube arrays (ZnO/TNTs) nanocomposites; however, there is still a paucity of reports on the construction of well-defined ZnO/TNTs heterostructure via efficient and easily accessible approach. In this work, drawing on a two-step anodization combined pyrolysis strategy, we attained a highly ordered ZnO/TNTs hybrid nanostructure. Combined with a collection of characterizations including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), diffusion reflectance spectrum (DRS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), we found that, in this coupling, in situ formed ZnO phases were uniformly grafted to TNTs framework giving rise to hybrid nanostructure, which is ascribed to cooperative interfacial interaction between polar TiO2 layer and ZnO precursor. The underlying interaction leading to judicious combination of TNTs and ZnO was unveiled by Fourier transformed infrared spectrum (FTIR) and XPS. Alternatively, it has been shown that ZnO nanocrystals distributed on the TNTs could serve as favorable hole channels and receptors for efficient separation of photoexcited charge carriers, which results in significantly enhanced photocatalytic performances of ZnO/TNTs heterostructure in comparison with pure TNTs, ZnO film, and P25 particulate film. Furthermore, it is found that the hybrid photocatalyst demonstrated excellent photostability. It is hoped that our work could present a straightforward paradigm for preparation of hierarchical semiconductor/1-D semiconductor heterostructures.

# Excited-State Dynamics in O6-Methylguanosine: Impact of O6-Methylation on the Relaxation Mechanism of Guanine Monomers\_2017

A simple chemical oxidation and ultrasound exfoliation method has been developed to synthesize the two-dimensional and ultrathin-layer materials—graphitic carbon nitride nanosheets (g-C3N4 NNs). The prepared ultrathin g-C3N4 NNs display strong fluorescence and stability, including good photostability and excellent antisalt ability. Herein, a new “on–off–on” fluorescent switching sensor is designed. The iron ion (Fe3+) has an ultrasensitive response to quench the fluorescence of g-C3N4 NNs based on the synergistic effect between inner filter effect and photoinduced electron transfer. The linear limit for Fe3+ was from 0.05 to 30 μmol L–1 with a detection limit of 0.018 μmol L–1. Meanwhile, the fluorescence of g-C3N4 NNs can recover through the redox reaction between Fe3+ and ascorbic acid (AA). In addition, the linear range for AA was from 0.2 to 112.5 μmol L–1 with a 0.086 μmol L–1 detection limit. The proposed method exhibited rapid response, excellent selectivity, wide detection range, and low detection limit for simultaneous analysis of Fe3+ and AA, and it was applied for the determination of Fe3+ and AA in water sample and human serum with satisfactory results.

# Construction of Highly Ordered ZnO–TiO2 Nanotube Arrays (ZnO/TNTs) Heterostructure for Photocatalytic Application\_2012

Highly oriented arrays of C, N, and S surface functionalized/surface doped ZnO Nanorods (NRs) were fabricated by a simple chemical bath deposition followed by wet chemical method. Surface functionalization significantly improved both the photocurrent and photostability of the ZnO NRs electrodes under visible-light irradiation along with the reduction in onset potential for water oxidation. The C-ZnO, N-ZnO, and S-ZnO NRs photoanodes exhibited 6.5, 5.5, and 3 times increase in photoelectrochemical water oxidation efficiency, respectively, as compared to that measured for pure ZnO NRs under visible-light illumination (10 mW·cm–2, wavelength >420 nm, 0.5 M Na2SO4). Surface engineered ZnO NRs also exhibited enhanced visible light harvesting efficiency and significantly quenched electron–hole recombination leading to greatly enhanced carrier separation. Surface doping remarkably tuned the electronic structure of the photoanodes changing the band position and band bending at electrode–electrolyte interface leading to low electrical resistance and fast charge transportation of the device boosting the PEC property. The study demonstrated that the surface functionalization could be a facile and general approach for oxide semiconductors to achieve an effective solution for high performance solar light-driven water splitting.

# Label-Free Simultaneous Analysis of Fe(III) and Ascorbic Acid Using Fluorescence Switching of Ultrathin Graphitic Carbon Nitride Nanosheets\_2018

A new intracellular O2 (icO2) sensing probe is presented, which comprises a nanoparticle (NP) formulation of a cationic polymer Eudragit RL-100 and a hydrophobic phosphorescent dye Pt(II)-tetrakis(pentafluorophenyl)porphyrin (PtPFPP). Using the time-resolved fluorescence (TR-F) plate reader set-up, cell loading was investigated in detail, particularly the effects of probe concentration, loading time, serum content in the medium, cell type, density, etc. The use of a fluorescent analogue of the probe in conjunction with confocal microscopy and flow cytometry analysis, revealed that cellular uptake of the NPs is driven by nonspecific energy-dependent endocytosis and that the probe localizes inside the cell close to the nucleus. Probe calibration in biological environment was performed, which allowed conversion of measured phosphorescence lifetime signals into icO2 concentration (μM). Its analytical performance in icO2 sensing experiments was demonstrated by monitoring metabolic responses of mouse embryonic fibroblast cells under ambient and hypoxic macroenvironment. The NP probe was seen to generate stable and reproducible signals in different types of mammalian cells and robust responses to their metabolic stimulation, thus allowing accurate quantitative analysis. High brightness and photostability allow its use in screening experiments with cell populations on a commercial TR-F reader, and for single cell analysis on a fluorescent microscope.

# Stable and Enhanced Visible-Light Water Electrolysis Using C, N, and S Surface Functionalized ZnO Nanorod Photoanodes: Engineering the Absorption and Electronic Structure\_2016

Designing a semiconductor CdS-based photocatalyst for H2 evolution from water with high activity and stability is extremely desirable for practical application. We report the important morphological and structural influence of MoS2 cocatalyst on the photocorrosion and photoactivity of CdS that is carpeted on a graphene (GR) surface. Homogeneous dispersion of MoS2 nanoparticles by a controlled photodeposition (PD) method produces the GR–CdS–MoS2 (PD) composite, which does not have the characteristic stacked layer structure of MoS2. However, this GR–CdS–MoS2 (PD) composite exhibits much higher activity and particularly antiphotocorrosion than the hydrothermal synthesized GR–CdS–MoS2 (HT) counterparts, which feature the characteristic MoS2 layer structure, toward photocatalytic water splitting under visible light irradiation. The characterization results indicate that homogeneous dispersion of tiny MoS2 for GR–CdS–MoS2 (PD) markedly improves the separation and transfer of charge carriers and provides the increased number of catalytic active sites afforded by the absence of the stacked layer structure of the MoS2 cocatalyst. This work provides direct evidence of the negative effect of the stacked layer structure of MoS2 on boosting the activity and photostability of CdS on the GR surface, which would guide the more rational use of MoS2 and GR as cocatalyst toward achieving a highly active and stable semiconductor-based composite photocatalyst for H2 evolution.

# Intracellular O2 Sensing Probe Based on Cell-Penetrating Phosphorescent Nanoparticles\_2011

The post-preparative irradiation of water-soluble thiol-stabilized ZnSe colloidal nanocrystals (NCs) leads to a strong increase of the photoluminescence quantum yield of UV blue emission. The altered photoluminescence properties of the colloidal samples have been explained previously by changes in particle composition, size, and surface modification accompanying irradiation. In this work, the charge carrier dynamics in NCs before and after irradiation treatment has been examined via femtosecond transient absorbance spectroscopy in the UV−visible spectral region. Upon adsorption of the electron acceptor methylviologen (MV2+), an ultrafast heterogeneous electron transfer from the conduction band of the nanocrystals to MV2+ is observed and studied. Therefore, the employment of the MV2+ helps to assign the observed dynamics to electron or hole relaxation processes. It is shown that a ZnSe/ZnS core/shell structure is formed during the post-preparative treatment. The transient absorbance measurements of the MV2+/NC system indicate that the formation of a shell results in the confinement of the hole to the core, while the electron is still delocalized throughout the entire core/shell structure. The confinement of the hole to the core also explains the strong increase of the photoluminescence quantum yield and the photostability of the NCs after post-preparative irradiation.

# Insight into the Effect of Highly Dispersed MoS2 versus Layer-Structured MoS2 on the Photocorrosion and Photoactivity of CdS in Graphene–CdS–MoS2 Composites\_2015

Photosensitization of polymers has been found to be important for a variety of purposes such as 1) Photopolymerization, 2) Photomodification (photo-grafting), 3) Photodegradation, and 4) Photostabilization (1). In commercial polymers photodegradation reactions are usually photosensitized by the presence of alien groups in the chain or by the presence of trace impurities (2,3).  
The first group of impurities is formed during storage and processing of polymers in the presence of air. Hydroperoxide, carbonyl and hydroxyl groups, and also unsaturated bonds, belong to the internal impurities. These groups are mainly formed during the moulding operations which require heat and pressure to shape the polymer into the required form. The thermal history of a polymer has been shown to have a marked effect on its subsequent photostability (4-8). Such groups may also be formed on the polymer surface during the exposure to sunlight.  
Second group of impurities consists of traces of compounds added

# Ultrafast Interfacial Charge Carrier Dynamics in ZnSe and ZnSe/ZnS Core/Shell Nanoparticles:  Influence of Shell Formation\_2008

In the present study, the results of comprehensive theoretical exploration on the nonradiative relaxation of three (hydroxyphenyl)imidazole-based organic compounds (abbreviated AHP, HPIP, and HPBI) in the gas phase are presented. Having small structural differences, the selected systems have commonalities in the excited state intramolecular proton transfer (ESIPT) process. The ground and S1 excited state potential energy profiles of titled systems have been determined on the basis of the RI-MP2 and RI-CC2 methods, and the effect of small structural distinctions on their photophysical characters will be extensively addressed. Although, in the presence of solvent, high fluorescence quantum yield is another characteristic of AHP and HPIP, owing to accessible conical intersections between the S1/S0 state potential energy profiles of both systems, nonradiative relaxation can be proposed as the most important feature of these two systems in the gas phase. These conical intersections are responsible for ultrafast deactivation of excited systems via internal conversions to the ground state. The nonradiative deactivation mechanism determined in this work deals with the remarkable photostability of the AHP and HPIP molecules.

# Photosensitized Degradation of Polymers\_1976

Nanometer-sized liposomes containing the oxygen-sensitive indicator tris(1,10-phenanthroline)ruthenium chloride (Ru(phen)3) in their internal compartment have been prepared and tested for their oxygen-sensing capabilities in aqueous solution. A standard injection technique, where a lipid mixture consisting of dimyristoylphospatidylcholine, cholesterol, and dihexadecyl phosphate (molar ratio 5:4:1) all dissolved in dry 2-propanol injected into an aqueous solution of 10 mM Ru(phen)3 under vortexing, is used to prepare the liposomes. A high uniformity of the liposomes is realized by extruding them back and forth through a 100-nm pore size polycarbonate membrane. TEM images of the liposomes, stained with uranyl acetate, show that the liposomes are unilamellar, round in shape, maintain high structural integrity, and average 70 nm in diameter. Dynamic light-scattering measurements support this observation. Under our experimental conditions, the entrapment efficiency of Ru(phen)3, defined as the ratio between the concentration of dye molecules encapsulated in the liposomes and the dye concentration in the solution used for liposome formation, is ∼1%. The liposomes show high stability with respect to dye leaking at room temperature for 8 days and high photostability when exposed to the excitation light. Individual liposomes are used to monitor the enzymatic oxidation of glucose by glucose oxidase in their vicinity. The newly prepared oxygen-sensitive liposomes can be applied for noninvasive oxygen analysis in tissues and single biological cells.

# Excited State Proton Transfer and Deactivation Mechanism of 2-(4′-Amino-2′-hydroxyphenyl)-1H-imidazo-[4,5-c]pyridine and Its Analogues: A Theoretical Study\_2016

Colloidal semiconductor nanocrystals are outstanding donors in energy transfer processes due to their unique size and shape dependent optical properties, their exceptional photostability, and chemical processability. We examine the dimensionality effect in energy transfer between single heterostructure nanocrystals of spherical and rod shape, serving as donors, and multiple dye molecules attached to their surface acting as acceptors. Förster resonant energy transfer (FRET) to individual dyes attached to the surface of a single nanocrystal is identified via step-like changes in both acceptor and donor emission, enabling to calculate the efficiency of energy transfer and distance of each acceptor individually. This offers a unique tool to study the surface chemistry of various nanocrystals. The dimensionality of the nanocrystals is reflected by the acceptors distribution, which enables to study the inner geometry of these heterostructures, such as the location of the seed and shell thickness. Additionally, the nanocrystals serve as an optical antenna that enhances the excitation and emission of the dye molecules through the FRET interaction. These measurements enable to gain deeper understanding of the energy transfer process between semiconductor nanocrystals of various geometries and dye molecules and promote its utilization for extremely sensitive sensing applications at the single molecule level.

# Dye-Encapsulating Liposomes as Fluorescence-Based Oxygen Nanosensors\_1998

Modern fluorescence imaging techniques have become essential tools to provide crucial insights in understanding complicated biological processes. Because of their unique optical properties (e.g., excellent photostability, high brightness, broad absorption, and narrow emission), inorganic quantum dots (QDs) have attracted great interest in fluorescence bioimaging. However, the intrinsic toxicity resulting from their heavy-metal components as well as the low-pH-induced fluorescence-quenching phenomenon has motivated researchers to explore novel fluorescent probes with the goal of overcoming these obstacles. In this work, we report the synthesis of two groups of organic fluorescent dots with aggregation-induced emission (AIE) characteristics that have a large Stokes shift, ensuring distinct emission spectra (green and red fluorescence) under single-wavelength excitation. Single-particle imaging experiments revealed the unique optical properties of such AIE dots, which outperform their commercially available inorganic QD counterpart in physical stability and brightness. Upon functionalization with a cell-penetrating peptide, the strong absorptivity, high brightness, good cellular-internalization efficiency, and low cytotoxicity of both the green and red AIE dots allow for the simultaneous discrimination of different populations of cancer cells both in culture medium and animal organs, which is of high importance for understanding cellular interactions during cancer metastasis. Considering the versatile surface functionalities endowed by the encapsulation matrix, a series of organic AIE dots with customized properties will provide prospective platforms to satisfy multifarious bioimaging tasks in the near future.

# Dimensionality Effects on Fluorescence Resonance Energy Transfer between Single Semiconductor Nanocrystals and Multiple Dye Acceptors\_2015

The rapidly increasing need for systems biology stimulates the development of supermultiplex (SM) methods for simultaneously labeling multiple biomolecules/cells with distinct colors. Here we report the development of DNA-engineered fractal nanoplasmonic labels with ultrahigh brightness and photostability for SM imaging in single cells. These color-resolvable nanoplasmonic labels have a uniform size of ∼50 nm with an inner hollow gap of ∼1 nm. The outer shell morphology is highly tunable with the tip aspect ratio covering the range of δ = 0.29–1.66, which supports SM plasmonic imaging exceeding the conventional fluorescence multiplexing limit. We demonstrate the use of these SM labels for quantitative imaging of receptor-mediated endocytosis and intracellular transport of multiple protein–NP structures in a single cell in real time. This SM-plasmonic method sheds light on elucidating complex interactions among protein–NPs in nanotoxicology and facilitates the development of novel nanomedicines for diagnosis and therapy.

# Organic Dots with Aggregation-Induced Emission (AIE Dots) Characteristics for Dual-Color Cell Tracing\_2013

Organic near-infrared (NIR) fluorescent probes have been recognized as an emerging class of materials exhibiting a great potential in advanced bioanalytical applications. However, synthesizing such organic probes that could simultaneously work in the NIR spectral range and have large Stokes shift, high stability in biological systems, and high photostability have been proven challenging. In this work, aggregation induced excimeric NIR emission in aqueous media was observed from a suitably substituted perylene monoimide (PeIm) dye. Controlled entrapment of the dye into pluronic F127 micellar system to preserve its monomeric green emission in aqueous media was also established. The aggregation process of the PeIm dye to form organic nanoparticles (NPs) was evaluated experimentally by the means of transmission electron microscope imaging as well as theoretically by the molecular dynamics simulation studies. Tuning the morphology along with the formation of colloidosomes by the controlled self-aggregation of PeIm NPs in aqueous suspension was demonstrated successfully. Finally, both excimeric and monomeric emissive PeIm NPs as well as PeIm colloidosomes were employed for the bioimaging in vitro.

# Fractal Nanoplasmonic Labels for Supermultiplex Imaging in Single Cells\_2019

In this study, we investigated the photoelectrochemical effect of guanidinium thiocyanate (GuSCN) in the base electrolyte composed of 1-methylbenzimidazole (0.45 M) and 3-methoxypropionitrile on the efficiency of electron injection (Φinj), interfacial recombination kinetics, and photovoltaic performance of dye-sensitized solar cells (DSCs). A significant increase in the photocurrent for DSCs with GuSCN was observed, which was higher than that for DSCs with the base electrolyte. The dependence of the short-circuit photocurrent density on the illumination intensity indicated that the large increase in Φinjcould be attributed to the positive shift in the flatband potential of the TiO2 electrode and could increase the electron injection yield. The results from electrochemical impedance spectroscopy (EIS) for DSCs indicated that guanidinium cation chemisorbed on the TiO2 surface could passivate the surface recombination sites and enhance the electron lifetime in the nanostructured TiO2 film to give an improved open-circuit photovoltage. The photostability of DSCs with 0.1 M GuSCN could retain over 98% of its initial photoelectric conversion efficiency value under one sun light soaking over the time of 3000 h. It is indicated that GuSCN chemisorbed on TiO2 surface could keep the interface of DSCs stable.

# Morphology Tuning of Self-Assembled Perylene Monoimide from Nanoparticles to Colloidosomes with Enhanced Excimeric NIR Emission for Bioimaging\_2016

Titanium dioxide (TiO2) deposited by atomic layer deposition (ALD) has been the most commonly used protection layer to enhance chemical and photoelectrochemical stabilities of photoelectrodes. In this study, we report a new electrochemical deposition method that can place a thin, conformal TiO2 coating layer on a photoelectrode. This method takes <1 min and may serve as a practical alternative to ALD for the deposition of a TiO2 layer. The uniform quality of the TiO2 protection layer was confirmed by demonstrating the chemical stability of the BiVO4/TiO2 electrode in strongly basic media (pH 12 and 13) where BiVO4 readily dissolves. More importantly, the high-quality TiO2 protection layer made it possible to comparatively investigate photoelectrochemical properties and stabilities of the BiVO4 and BiVO4/TiO2 electrodes, which was critical to elucidate the effect that the chemical instability of BiVO4 in basic media has on the rate of photocorrosion. Systematic photoelectrochemical studies for sulfite oxidation and water oxidation provided a coherent understanding of how the interplay among the relative rates of interfacial charge transfer, surface recombination, and photocorrosion affects the photocurrent generation and photostability of BiVO4. On the basis of this understanding, stable photocurrent generation for water oxidation could be achieved at pH 12 over 20 h using a BiVO4/TiO2/FeOOH/NiOOH electrode where FeOOH/NiOOH served as oxygen evolution catalyst. The results and discussion contained in this study provide new insights into the understanding of photocurrent decay caused by photocorrosion involving dissolution, enabling the development of effective strategies to achieve stable photocurrent generation.

# Photoelectrochemical Effects of Guanidinium Thiocyanate on Dye-Sensitized Solar Cell Performance and Stability\_2009

Surgical resection is recognized as a mainstay in the therapy of malignant brain tumors. In clinical practice, however, surgeons face great challenges in identifying the tumor boundaries due to the infiltrating and heterogeneous nature of neoplastic tissues. Contrast-enhanced magnetic resonance imaging (MRI) is extensively used for defining the brain tumor in clinic. Disappointingly, the commercially available (MR) contrast agents show the transient circulation lifetime and poor blood–brain barrier (BBB) permeability, which seriously hamper their abilities in tumor visualization. In this work, red fluorescent carbonized polymer dots (CPDs) were systematically investigated with respect to their BBB-penetration ability. In summary, CPDs possess long excitation/emission wavelengths, low toxicity, high photostability, and excellent biocompatibility. CPDs exhibit high internalization in glioma cells in time- and dose-dependent procedures, and internalized CPDs locate mainly in endolysosomal structures. In vitro and in vivo studies confirmed the BBB permeability of CPDs, contributing to the early stage diagnosis of brain disorders and the noninvasive visualization of the brain tumor without compromised BBB. Furthermore, owing to the high tumor to normal tissue ratio of CPDs under ex vivo conditions, our nanoprobe holds the promise to guide brain-tumor resection by real-time fluorescence imaging during surgery.

# Enabling Solar Water Oxidation by BiVO4 Photoanodes in Basic Media\_2018

In recent years, semiconducting polymer dots (Pdots) have emerged as a novel class of extraordinarily bright fluorescent probes with burgeoning applications in bioimaging and sensing. While the desire for near-infrared (NIR)-emitting agents for in vivo biological applications increases drastically, the direct synthesis of semiconducting polymers that can form Pdots with ultrahigh fluorescence brightness is extremely lacking due to the severe aggregation-caused quenching of the NIR chromophores in Pdots. Here we describe the synthesis of dithienylbenzoselenadiazole (DBS)-based NIR-fluorescing Pdots with ultrahigh brightness and excellent photostability. More importantly, the fluorescence quantum yields of these Pdots could be effectively increased by the introduction of long alkyl chains into the thiophene rings of DBS to significantly inhibit the aggregation-caused emission quenching. Additionally, these new series of DBS-based Pdots can be excited by a commonly used 488 nm laser and show a fluorescence quantum yield as high as 36% with a Stokes shift larger than 200 nm. Single-particle analysis indicates that the per-particle brightness of the Pdots is at least 2 times higher than that of the commercial quantum dot (Qdot705) under identical laser excitation and acquisition conditions. We also functionalized the Pdots with carboxylic acid groups and then linked biomolecules to Pdot surfaces to demonstrate their capability for specific cellular labeling without any noticeable nonspecific binding. Our results suggest that these DBS-based NIR-fluorescing Pdots will be very practical in various biological imaging and analytical applications.

# Noninvasive Brain Tumor Imaging Using Red Emissive Carbonized Polymer Dots across the Blood–Brain Barrier\_2018

Porphyrin rings CZ4, CZ6, and CZ8 that respectively comprise four, six, and eight porphyrins, immobilized in a thin PMMA film, have been investigated using single molecule fluorescence spectroscopy with a focus on the influences of the overall structural rigidity as the ring size of porphyrin array increases. Neighboring porphyrin moieties were linked directly to enhance through-bond electronic interactions and, as a consequence, efficient excitation energy migration processes like the natural LH2 complex. Unlike the ensemble study, the single molecule study using confocal microscopy could eliminate the averaging effect, and consequently provide detailed information on individual molecular behaviors. Indeed, in solution, as a dihedral angle between neighboring porphyrins decreases in the order of CZ6 > CZ8 > CZ4, red-shifted Q-absorption bands and faster excitation energy hopping rates were observed. However, at the single molecule level, we found that they show longer survival times, less frequent on−off behaviors, narrower fluorescence lifetime distributions, and high relative single molecular brightness in the order of CZ8 > CZ6 > CZ4, by recording fluorescence intensity trajectories. Especially, CZ4 reveals high photostability with its rigid structure, and about 3 porphyrin units among the 4 chromophores-constituted molecule behave as a collective coherent domain. Thus, our results single out CZ4 as a potential and promising candidate for application in artificial light harvesting solid-state devices.

# Near-Infrared Fluorescent Semiconducting Polymer Dots with High Brightness and Pronounced Effect of Positioning Alkyl Chains on the Comonomers\_2014

Luminescent radicals have various applications because they simultaneously possess optoelectronic, electronic, and magnetic properties. Despite the development of some luminescent tris(2,4,6-trichlorophenyl)methyl (TTM)-based radicals, all the substituents directly attached to the TTM skeleton are electron-donating groups. Herein, the electron-withdrawing group is first attached to a p carbon of the parent TTM radical, and two novel stable open-shell adducts based on the benzimidazole unit with red-orange emission are obtained. Their photophysical properties, photochemical stabilities, and electroluminescent performances are fully investigated. Because of the introduction of the benzimidazole unit, the intramolecular charge transfer property of D–A type molecules is suppressed to a large extent, and the delocalization of the sole electron is strengthened. Both radicals exhibit largely improved photostability compared to that of the TTM core. High PL quantum yields (ΦF) of 0.39 and 0.36 in doped films are achieved, which are among the highest values for luminescent radicals. Extremely high-voltage-durable characteristic is demonstrated in the organic light-emitting diodes utilizing them as emitters. One device has a maximal external quantum efficiency that even exceeds the classical theoretical upper limit of 5%.

# Fluorescence Dynamics of Directly Meso−Meso Linked Porphyrin Rings Probed by Single Molecule Spectroscopy\_2009

Allylamine-functionalized silicon quantum dots (ASQDs) of high photostability are synthesized by a robust inverse micelle method to use the material as a fluorescent probe for selective recognition of thiocyanate (a biomarker of a smoker and a nonsmoker). The synthesized ASQDs were characterized by absorption, emission, and Fourier transform infrared spectroscopy. Surface morphology is studied by transmission electron microscopy and dynamic light scattering. The synthesized material exhibits desirable fluorescence behavior with a high quantum yield. A selective and accurate (up to 10–10 M) method of sensing of thiocyanate anion is developed based on fluorescence amplification and quenching of ASQDs. The sensing mechanism is investigated and interpreted with a crystal clear mechanistic approach through the modified Stern–Volmer plot. The developed material and the method is applied to recognize the anion in the human blood sample for identification of the degree of smoking. The material deserves high potentiality in the field of bio-medical science.

# Novel Luminescent Benzimidazole-Substituent Tris(2,4,6-trichlorophenyl)methyl Radicals: Photophysics, Stability, and Highly Efficient Red-Orange Electroluminescence\_2017

Immobilization procedures, intended to enable prolonged observation of single molecules by fluorescence microscopy, may generate heterogeneous microenvironments, thus inducing heterogeneity in the molecular behavior. On that account, we propose a straightforward surface preparation procedure for studying chemical reactions on the single-molecule level. Sensor fluorophores were developed, which exhibit dual-emissive characteristics in a homogeneously catalyzed showcase reaction. These molecules undergo a shift of fluorescence wavelength of about 100 nm upon Pd(0)-induced deallylation in the Tsuji–Trost reaction, allowing for separate visualization of the starting material and product. Whereas a simultaneous immobilization of dye and inert silane leads to strongly polydisperse reaction kinetics, a consecutive immobilization routine with deposition of dye molecules as the last step provides substrates underlying the kinetics of ensemble experiments. Also, the found kinetics are unaffected by the chemical variation of inert silanes, nearly uniform, and therefore well reproducible. Additional parameters like photostability, signal-to-noise ratio, dye-molecule density, and spatial distribution of dye molecules are, as well, hardly affected by surface modification in the successive immobilization scheme.

# Silicon Quantum Dot-Based Fluorescent Probe: Synthesis Characterization and Recognition of Thiocyanate in Human Blood\_2018

The addition of photosensitizers to water can accelerate disinfection in sunlight-based systems by enhancing oxidation of target compounds through direct reaction with the excited sensitizer or through production of another oxidant, such as singlet oxygen (1O2). The kinetics of the oxidation of selected amino acids in the presence of the sensitizer riboflavin (Vitamin B2), its primary photoproduct lumichrome, and its derivative riboflavin tetraacetate (2′,3′,4′,5′-tetraacetylriboflavin; RTA) were quantified and the mechanisms of reaction were determined during exposure to 365 ± 9 nm light. 1O2-mediated reactions contributed to the rapid photodegradation of the four amino acids, but its contribution was sensitizer-dependent and varied from 5.4−10.2% for tyrosine, 7.1–12.4% for tryptophan, 18.7–69.0% for methionine, and 64.7–100.2% for histidine. Riboflavin was subject to rapid photodegradation (t1/2 <8 min), while the half-lives of lumichrome and RTA were 100 and 30 times longer, respectively. Lumichrome and RTA also were more efficient 1O2 sensitizers (quantum yield (Φ) = 0.63 and 0.66) compared to riboflavin (Φ = 0.48). Of the three flavin-based compounds, RTA shows the most promise as a sensitizer in sunlight-based disinfection systems because it absorbs both visible and UV light, is an efficient 1O2 sensitizer, is a strong oxidant in its triplet state, and exhibits greater photostability.

# Surface Preparation for Single-Molecule Chemistry\_2019

Depth-dependent growth of perovskite crystals remains challenging for high-performance perovskite solar cells made by a two-step spin-coating method. Effective morphology engineering approaches that enable depth-independent perovskite crystals growth and facile characterization technique to monitor subtle yet influential accompanying changes are urgently required. Here, a porous and intercrossed PbI2–(CsI)0.15 nanorods scaffold is prepared by integrating CsI incorporation with toluene dripping in ambient air, and the underlying mechanism is uncovered. With this porous scaffold and moisture-assisted thermal annealing, depth-independent growth of FA0.85Cs0.15PbI3 is achieved, as evidenced in the photoluminescent (PL) spectra acquired by exciting the perovskite film from the top and bottom individually. It is of broad interest that PL spectroscopy is demonstrated as a sensitive technique to monitor the depth-dependent growth of perovskite. Moreover, the resulting inverted planar FA0.85Cs0.15PbI3 perovskite solar cells deliver an efficiency of 16.85%, along with superior thermal and photostability. By incorporating 2% large-sized diammonium cation, propane-1,3-diammonium, the efficiency is further increased to 17.74%. Our work not only proposes a unique porous PbI2–(CsI)0.15 nanorods scaffold to achieve high-quality perovskite films in a two-step method but also highlights the distinctive advantage of PL spectroscopy in monitoring the depth-dependent quality of perovskite films.

# Photosensitized Amino Acid Degradation in the Presence of Riboflavin and Its Derivatives\_2011

A collection of nine pentamethine indocyanine dyes was synthesized, and the photophysical characteristics relevant to applications in cell biology and single molecule detection were analyzed in detail. Substituents at the aromatic system covering the auxochromic series and substitutions in the polymethine chain were investigated with respect to absorption and emission spectra, fluorescence lifetimes, fluorescence quantum yields, and fluorescence autocorrelations. Substitutions in the polymethine chain increased the nonradiative energy dissipation of the excited singlet state and decreased the fluorescence quantum yield, relative to the unsubstituted compound. For substituents at the aromatic rings the fluorescence quantum yield negatively correlates with the position of the substituents in the auxochromic series -SO3-, -H, -F, -CH3. Compounds with sulfonic acid groups or halogen atoms attached to the indolenine systems had the highest fluorescence quantum yields. The compound S0387 had nearly 70% of the quantum yield of Cy5 and comparable photostability. The free carboxylic acid of S0387 was attached to peptides in high yield and purity by established procedures of solid-phase synthesis. The dye-labeled peptides did not aggregate or bind to tissue culture cells and proteins unspecifically. The indocyanine dye S0387 is therefore an attractive new fluorophore for in vitro and cell-based detection of receptor ligand interaction at nanomolar concentrations by flow cytometry, fluorescence correlation spectroscopy, and laser scanning microscopy.

# Porous and Intercrossed PbI2–CsI Nanorod Scaffold for Inverted Planar FA–Cs Mixed-Cation Perovskite Solar Cells\_2019

An efficient and stable heterojunction photoanode for solar water oxidation was fabricated by hybridization of WO3 and conducting polymers (CPs). Organic/inorganic hybrid photoanodes were readily prepared by the electropolymerization of various CPs and the codeposition of tetraruthenium polyoxometalate (Ru4POM) water-oxidation catalysts (WOCs) on the surface of WO3. The deposition of CPs, especially polypyrrole (PPy) doped with Ru4POM (PPy:Ru4POM), resulted in a remarkably improved photoelectrochemical performance by the formation of a WO3/PPy p–n heterojunction and the incorporation of efficient Ru4POM WOCs. In addition, there was also a significant improvement in the photostability of the WO3-based photoanode after the deposition of the PPy:Ru4POM layer due to the suppression of the formation of hydrogen peroxide, which was responsible for corrosion. This study provides insight into the design and fabrication of novel photosynthetic and photocatalytic systems with excellent performance and stability through the hybridization of organic and inorganic materials.

# Structure Property Analysis of Pentamethine Indocyanine Dyes:  Identification of a New Dye for Life Science Applications\_2004

Without changing underlying plasmonic substrate designs, tunable fluorescence enhancement is achieved by varying surrounding fluidic refractive indices on a colorimetric plasmonic substrate of periodic Au nanocup arrays. When comparing the emission characteristics of two fluorophores on the plasmonic surface, HEX with green emission and TEX with red emission, tuning the plasmonic resonance wavelength matched with the emission band of fluorophores is verified as a key factor for the largest fluorescence amplification. Even though the plasmonic nanocup array substrate is already capable of enhancing fluorescence emission compared to that on the Au film, further enhancement by 6.93-fold for HEX at 1.36 refractive index unit (RIU) and 7.12-fold for TEX at 1.45 RIU, both from 1 RIU, is accomplished on the same nanoplasmonic device. The numerical calculations of the quantum efficiency and the radiative decay rate show the same response with the experimental fluorescence emission variations under fluidic refractive index variations. The lifetime reduction of HEX and TEX from solution states proves the enhanced photostability on the plasmonic surface. These findings on optofluidically tuned fluorescence enhancement guide a pathway on multiplexed detection of local molecular binding on targets tagged with fluorescence dyes through a subsequent refractive index change on the nanoplasmonic substrate.

# WO3/Conducting Polymer Heterojunction Photoanodes for Efficient and Stable Photoelectrochemical Water Splitting\_2018

The molecular structure and photochemistry of 5-thiosaccharyl-1-methyltetrazole (TSMT) were studied by means of matrix-isolation FTIR spectroscopy, X-ray crystallography, and theoretical calculations. The calculations predicted two conformers of TSMT that differ in energy by more than 15 kJ mol–1. The infrared spectrum of TSMT isolated in solid argon was fully assigned on the basis of the spectrum calculated (O3LYP/6-311++G(3df,3pd)) for the most stable conformer. In the crystal, TSMT molecules were found to assume the same conformation as for the isolated molecule, with each molecule forming four hydrogen bonds with three neighboring molecules, leading to a network of TSMT oligomers. Upon UV (λ = 265 nm) irradiation of the matrix-isolated TSMT, two photodegradation pathways were observed, both arising from cleavage of the tetrazolyl ring. Pathway a involves cleavage of the N1–N2 and N3–N4 bonds with extrusion of N2, leading to photostable diazirine and thiocarbodiimide derivatives. The photostability of the photoproduced diazirine under the conditions used precluded its rearrangement to the nitrile imine, as reported for 5-phenyltetrazole by Bégué et al. ( J. Am. Chem. Soc. 2012, 134, 5339). Pathway b involves cleavage of the C5–N1 and N4–N3 bonds, leading to a thiocyanate and methyl azide, the latter undergoing subsequent fragmentation to give CNH.

# Colorimetric Effect of Gold Nanocup Arrays on Fluorescence Amplification\_2015

A two-photon absorbing (2PA) and aggregation-enhanced near-infrared (NIR) emitting pyran derivative, encapsulated in and stabilized by silica nanoparticles (SiNPs), is reported as a nanoprobe for two-photon fluorescence microscopy (2PFM) bioimaging that overcomes the fluorescence quenching associated with high chromophore loading. The new SiNP probe exhibited aggregate-enhanced emission producing nearly twice as strong a signal as the unaggregated dye, a 3-fold increase in two-photon absorption relative to the DFP in solution, and approximately 4-fold increase in photostability. The surface of the nanoparticles was functionalized with a folic acid (FA) derivative for folate-mediated delivery of the nanoprobe for 2PFM bioimaging. Surface modification of SiNPs with the FA derivative was supported by zeta potential variation and 1H NMR spectral characterization of the SiNPs as a function of surface modification. In vitro studies using HeLa cells expressing a folate receptor (FR) indicated specific cellular uptake of the functionalized nanoparticles. The nanoprobe was demonstrated for FR-targeted one-photon in vivo imaging of HeLa tumor xenograft in mice upon intravenous injection of the probe. The FR-targeting nanoprobe not only exhibited highly selective tumor targeting but also readily extravasated from tumor vessels, penetrated into the tumor parenchyma, and was internalized by the tumor cells. Two-photon fluorescence microscopy bioimaging provided three-dimensional (3D) cellular-level resolution imaging up to 350 μm deep in the HeLa tumor.

# Structure and Photochemistry of a Saccharyl Thiotetrazole\_2014

Visualizing proton-transfer processes at the nanoscale is essential for understanding the reactivity of zeolite-based catalyst materials. In this work, the Brønsted-acid-catalyzed oligomerization of styrene derivatives was used for the first time as a single molecule probe reaction to study the reactivity of individual zeolite H-ZSM-5 crystals in different zeolite framework, reactant and solvent environments. This was accomplished via the formation of distinct dimeric and trimeric fluorescent carbocations, characterized by their different photostability, as detected by single molecule fluorescence microscopy. The oligomerization kinetics turned out to be very sensitive to the reaction conditions and the presence of the local structural defects in zeolite H-ZSM-5 crystals. The remarkably photostable trimeric carbocations were found to be formed predominantly near defect-rich crystalline regions. This spectroscopic marker offers clear prospects for nanoscale quality control of zeolite-based materials. Interestingly, replacing n-heptane with 1-butanol as a solvent led to a reactivity decrease of several orders and shorter survival times of fluorescent products due to the strong chemisorption of 1-butanol onto the Brønsted acid sites. A similar effect was achieved by changing the electrophilic character of the para-substituent of the styrene moiety. Based on the measured turnover rates we have established a quantitative, single turnover approach to evaluate substituent and solvent effects on the reactivity of individual zeolite H-ZSM-5 crystals.

# Folate Receptor-Targeted Aggregation-Enhanced Near-IR Emitting Silica Nanoprobe for One-Photon in Vivo and Two-Photon ex Vivo Fluorescence Bioimaging\_2011

Herein, we reported a red-emitting probe (E)-4-(2-(8-hydroxy-julolidine-9-yl)vinyl)-1-methylpyridin-1-ium iodide (HJVPI) on a rotor mechanism with an ultrahigh signal-to-noise ratio. HJVPI could give high-fidelity fluorescent images of mitochondria in living immortalized and normal cells and be suitable for IR excitation source of two-photon microscopy and various excitation sources of confocal microscopy. As a rotor, its single/two-photon fluorescence intensities directly depended on environmental viscosity. And, as a mitochondrial probe, it displayed much larger two-photon absorption cross sections in comparison with commercial MitoTracker Green FM and MitoTracker Red FM. Moreover, the fact that living cells stained by HJVPI still possessed physiological function could also be confirmed: (1) MTT assay demonstrated that the mitochondria of cells stained retained their electron mediating ability and (2) double assay of HJVPI and SYTOX Blue nucleic acid stain (S-11348) showed that the plasma membrane of the cells stained was still intact. In addition, HJVPI possessed a number of beneficial properties in bioimaging such as good membrane permeability, high photostability, and excellent counterstain compatibility with Hoechst 33342. Related mechanism research suggested that its localization property was dependent on the mitochondrial membrane potential in living cells. All its remarkable properties can extend the investigation on mitochondria in a biological context.

# Single Molecule Nanospectroscopy Visualizes Proton-Transfer Processes within a Zeolite Crystal\_2016

Lead halide perovskites hold promise for photonic devices, due to their superior optoelectronic properties. However, their use is limited by poor stability and toxicity. We demonstrate enhanced water and light stability of high-surface-area colloidal perovskite nanocrystals by encapsulation of colloidal CsPbBr3 quantum dots into matched hydrophobic macroscale polymeric matrices. This is achieved by mixing the quantum dots with presynthesized high-molecular-weight polymers. We monitor the photoluminescence quantum yield of the perovskite–polymer nanocomposite films under water-soaking for the first time, finding no change even after >4 months of continuous immersion in water. Furthermore, photostability is greatly enhanced in the macroscale polymer-encapsulated nanocrystal perovskites, which sustain >1010 absorption events per quantum dot prior to photodegradation, a significant threshold for potential device use. Control of the quantum dot shape in these thin-film polymer composite enables color tunability via strong quantum-confinement in nanoplates and significant room temperature polarized emission from perovskite nanowires. Not only does the high-molecular-weight polymer protect the perovskites from the environment but also no escaped lead was detected in water that was in contact with the encapsulated perovskites for months. Our ligand-passivated perovskite-macroscale polymer composites provide a robust platform for diverse photonic applications.

# Red-Emitting Mitochondrial Probe with Ultrahigh Signal-to-Noise Ratio Enables High-Fidelity Fluorescent Images in Two-Photon Microscopy\_2015

Nanoantennas are well-known for their effective role in fluorescence enhancement, both in excitation and emission. Enhancements of 3–4 orders of magnitude have been reported. Yet in practice, the photon emission is limited by saturation due to the time that a molecule spends in singlet and especially triplet excited states. The maximal photon stream restricts the attainable enhancement. Furthermore, the total number of photons emitted is limited by photobleaching. The limited brightness and observation time are a drawback for applications, especially in biology. Here we challenge this photon limit, showing that nanoantennas can actually increase both saturation intensity and photostability. So far, this limit-shifting role of nanoantennas has hardly been explored. Specifically, we demonstrate that single light-harvesting complexes, under saturating excitation conditions, show over a 50-fold antenna-enhanced photon emission stream, with 10-fold more total photons, up to 108 detected photons, before photobleaching. This work shows yet another facet of the great potential of nanoantennas in the world of single-molecule biology.

# Encapsulation of Perovskite Nanocrystals into Macroscale Polymer Matrices: Enhanced Stability and Polarization\_2016

The two complementary technologies of colloidal upconverting nanoemitters and maskless photolithography are exploited to fabricate nanoengineered optically active surfaces for anticounterfeiting applications based on the multiphoton absorption phenomenon in lanthanide nanocomposites with a visualization wavelength in the NIR. It is demonstrated that the unique optical, thermal, and temporal characteristics of these versatile upconverting surface distinguishes them from their counterparts. A unique behavior that is captured is the ability to actively tune their emission color by modifying the pumping power, temperature, and excitation frequency. A new low-cost negative photoresist is employed for implementation of maskless photolithography of single- and double-color labels using two efficient upconverting nanocomposites based on NaYF4:Yb3+, Er3+ and NaYF4:Yb3+, Tm3+ nanoemitters. In addition, it is shown that the detectability of the proposed anticounterfeiting approach can be carried out using just a smartphone. Each of the emission peaks of the upconversion nanoparticles is associated with a different multiphoton absorption mechanism and their thermosensitivity varies from one peak to another. Furthermore, their photoluminescent color changes by scanning the excitation beam impinging on the surfaces composed of both upconversion nanoparticles doped in the UV-curable resist. Long-term photostability of these surfaces under continuous excitation by a high power laser makes them a promising nanoemitters for the next generation of anticounterfeiting labels.

# Pushing the Photon Limit: Nanoantennas Increase Maximal Photon Stream and Total Photon Number\_2016

Interest and effort toward new materials for rewritable paper have increased dramatically because of the exciting advantages for sustainable development and better nature life cycle. Inspired by how nature works within living systems, herein, we have used fluorans, as a concept verification, to endow original acidochromic, basochromic or photochromic molecules with broader properties, such as switchable with solvent, water, heat, electricity, stress, other force, etc., via simplified methods (i.e., via variation of submolecular structure or microenvironments). The hydrochromic visual change and reversible behavior of selected molecules have been explored, and the primary mechanism at the atomic or subatomic level has been hypothesized. In addition, several newly demonstrated hydrochromic fluorans have been utilized for water-jet rewritable paper (WJRP), which exhibit great photostability, high hydrochromic contrast, and fast responsive rate and which can be reused at least 30 times without significant variation. The water-jet prints have good resolution and various colors and can keep legibility after a few months or years. This improved performance is a major step toward practical applications of WJRP.

# Upconverting Nanoengineered Surfaces: Maskless Photolithography for Security Applications\_2019

A series of nickel complexes of 2-(arylazo)pyridine have been synthesized, and the precise structure and stoichiometry of the complexes are controlled by the use of different metal precursors. Molecular and electronic structures of the isolated complexes are scrutinized thoroughly by various spectroscopic techniques, single crystal X-ray crystallography, and density functional theory (DFT). Two different classes of Ni(II) complexes are identified where the ligands bind as neutral or anion radicals in the respective metal complexes. These are shown to be chemically interconvertible, and their characterization confirmed that the redox series is entirely ligand-centered without affecting the bivalent oxidation state of the metal ion. An efficient method of Ni(II) catalyzed N-arylation of 2-(arylazo)pyridine substrates has been elaborated. The chemical reactions have led to isolation of strongly fluorescent 2-pyridyl-substituted hydrazine derivatives, which have been characterized thoroughly. Three-dimensional X-ray structure of a hydrazine molecule, 2-(2-(naphthalen-1-yl)-2-phenylhydrazinyl)pyridine, is reported. Isolated hydrazines satisfy all the prerequisites of an ideal dye with moderate absorptive property, large Stokes shift, high quantum yields, and high photostability.

# Endowing Hydrochromism to Fluorans via Bioinspired Alteration of Molecular Structures and Microenvironments and Expanding Their Potential for Rewritable Paper\_2017

Acid–base disorders disrupt proper cellular functions, which are associated with diverse diseases. Development of highly sensitive pH probes being capable of detecting and monitoring the minor changes of pH environment in living systems is of considerable interest to diagnose disease as well as investigate biochemical processes in vivo. We report herein two novel high-resolution ratiometric two-photon (TP) fluorescent probes, namely, PSIOH and PSIBOH derived from carbazole–oxazolidine π-conjugated system for effective sensing and monitoring acid pH in a biological system. Remarkably, PSIOH exhibited the largest emission shift of ∼169 nm from 435 to 604 nm upon pH changing from basic to acidic with an ideal pKa value of 6.6 within a linear pH variation range of 6.2–7.0, which is highly desirable for high-resolution tracking and imaging the minor fluctuation of pH in live cells and tissues. PSIOH also exhibits high pH sensitivity, excellent photostability, and reversibility as well as low cytotoxicity. More importantly, this probe was successfully applied to (i) sense and visualize the pH alteration in HeLa cells caused by various types of exogenous stimulation and (ii) detect and differentiate cancer and tumors in liver tissues and a mouse model, realizing its practical in vitro and in vivo applications.

# Ligand-Centered Redox in Nickel(II) Complexes of 2-(Arylazo)pyridine and Isolation of 2-Pyridyl-Substituted Triaryl Hydrazines via Catalytic N-Arylation of Azo-Function\_2014

Properties of a series of acetylene-linked perylene bisimide (PBI) macrocycles with different ring size composed of three to six PBI dyes were investigated by atomic force microscopy (AFM) and single-molecule fluorescence spectroscopy in a condensed phase. It was demonstrated that the structures of PBI cyclic arrays (CNs, N = 3, 4, 5, and 6) become distorted with increasing the ring size through molecular dynamics (MD) simulations (PM6-DH2 method) and AFM height images of CNs on highly ordered pyrolytic graphite (HOPG) surface. The MD simulations showed that only C5 and C6 rings are highly flexible molecules whose planarization goes along with a significant energetic penalty. Accordingly, both molecules did not show ordered adlayers on a HOPG surface. In contrast, C3 and C4 are far more rigid molecules leading to well-ordered hexagonal (C3) and rectangular (C4) 2D lattices. At the single-molecule level, we showed that the fluorescence properties of single CNs are affected by the structural changes. The fluorescence lifetimes of CNs became shorter and their distributions became broader due to the structural distortions with increasing the ring size. Furthermore, the CNs of smaller ring size exhibit a higher photostability and an efficient excitation energy transfer (EET) due to the more well-defined and planar structures compared to the larger CNs. Consequently, these observations provide evidence that not only PBI macrocycles are promising candidates for artificial light-harvesting systems, but also the photophysical properties of CNs are strongly related to the structural rigidity of CNs.

# A Zero Cross-Talk Ratiometric Two-Photon Probe for Imaging of Acid pH in Living Cells and Tissues and Early Detection of Tumor in Mouse Model\_2018

Cytosine methylation and demethylation play crucial roles in understanding the genomic DNA expression regulation. The epigenetic modification of cytosine and its continuous oxidative products are called the “new four bases of DNA” including 5-methylcytosine (5mC), 5-hydroxymethylcytosine (5hmC), 5-formylcytosine (5fC), and 5-carboxylcytosine (5caC). However, compared to the abundant studies on the classical DNA bases, the photophysical and photochemical properties of those new bases have not yet aroused people’s excessive attention. In this contribution, a systematic study on the nonradiative decay and photochemical pathways via excited states or conical intersections upon photoexcitation has been explored through high-level computational approaches such as the complete active space self-consistent field method, complete active space with second-order perturbation theory, and density functional theory. Pathways like the ring-distortion deactivation, hydrogen dissociation, hydrogen transfer, and also Norrish type I and II photochemical reactions have been investigated, and it was proposed that intersystem crossing from the S1 state to the T1 state is the most effective route for 5fC. For 5caC, ring-pucking and intramolecular isomerism are effective deactivation ways at both neutral and protonated forms. In the meantime, the influences of two important environmental factors, the solution and acidic environment (i.e., the protonated state), were also considered in this study. From the theoretical perspective, the initial properties of the photostability and photochemical reactivity for 5fC and 5caC have become a crucial aspect to facilitate a further comprehension of their potential role in gene regulation and transcription.

# Structure–Property Relationship of Perylene Bisimide Macrocycles Probed by Atomic Force Microscopy and Single-Molecule Fluorescence Spectroscopy\_2013

Measuring pH in living cells is of great importance for better understanding cellular functions as well as providing pivotal assistance for early diagnosis of diseases. In this work, we report the first use of a novel kind of label-free carbon dots for intracellular ratiometric fluorescence pH sensing. By simple one-pot hydrothermal treatment of citric acid and basic fuchsin, the carbon dots showing dual emission bands at 475 and 545 nm under single-wavelength excitation were synthesized. It is demonstrated that the fluorescence intensities of the as-synthesized carbon dots at the two emissions are pH-sensitive simultaneously. The intensity ratio (I475 nm/I545 nm) is linear against pH values from 5.2 to 8.8 in buffer solution, affording the capability as ratiometric probes for intracellular pH sensing. It also displays that the carbon dots show excellent reversibility and photostability in pH measurements. With this nanoprobe, quantitative fluorescence imaging using the ratio of two emissions (I475 nm/I545 nm) for the detection of intracellular pH were successfully applied in HeLa cells. In contrast to most of the reported nanomaterials-based ratiometric pH sensors which rely on the attachment of additional dyes, these carbon-dots-based ratiometric probes are low in toxicity, easy to synthesize, and free from labels.

# Theoretical Studies on the Photophysics and Photochemistry of 5-Formylcytosine and 5-Carboxylcytosine: The Oxidative Products of Epigenetic Modification of Cytosine in DNA\_2018

Far-red and near-infrared (NIR) fluorescent materials possessing the characteristics of strong two-photon absorption and aggregation-induced emission (AIE) as well as specific targeting capability are much-sought-after for bioimaging and therapeutic applications due to their deep penetration depth and high resolution. Herein, a series of dipolar far-red and NIR AIE luminogens with a strong push–pull effect are designed and synthesized. The obtained fluorophores display bright far-red and NIR solid-state fluorescence with a high quantum yield of up to 30%, large Stokes shifts of up to 244 nm, and large two-photon absorption cross-sections of up to 887 GM. A total of three neutral AIEgens show specific lipid droplet (LD)-targeting capability, while the one with cationic and lipophilic characteristics tends to target the mitochondria specifically. All of the molecules demonstrate good biocompatibility, high brightness, and superior photostability. They also serve as efficient two-photon fluorescence-imaging agents for the clear visualization of LDs or mitochondria in living cells and tissues with deep tissue penetration (up to 150 μm) and high contrast. These AIEgens can efficiently generate singlet oxygen upon light irradiation for the photodynamic ablation of cancer cells. All of these intriguing results prove that these far-red and NIR AIEgens are excellent candidates for the two-photon fluorescence imaging of LDs or mitochondria and organelle-targeting photodynamic cancer therapy.

# Label-Free Carbon-Dots-Based Ratiometric Fluorescence pH Nanoprobes for Intracellular pH Sensing\_2016

A synthetic method is proposed for the preparation of micrometer-sized hybrid materials in the form of highly stable, water-soluble, porous, and intrinsic fluorescent vaterites. This is an easy, cost-effective, and polymer-free synthetic method, that is, free of any supplementary complex synthetic or natural macromolecular stabilizers. This method uses a double decomposition reaction to introduce fluorescence as an intrinsic property into the vaterite scaffold, through either organic dyes or dihydrolipoic acid coated core/shell CdSe/ZnS quantum dots. The resulting hybrid scaffold has excellent brightness, photostability, thermal stability, and pH stability. Combined with a large loading surface offered by the vaterite scaffold and the ease of chemical functionalization provided by the water-soluble quantum dots, the obtained hybrid scaffolds show promise in biological applications. Fluorescence imaging and fluorescence-resonance-energy-transfer-based sensing of proteins based on these hybrid materials is illustrated with these hybrid materials at the single-particle level.

# Bright Near-Infrared Aggregation-Induced Emission Luminogens with Strong Two-Photon Absorption, Excellent Organelle Specificity, and Efficient Photodynamic Therapy Potential\_2018

Systematic comparisons among the oxazinone, quinazoline, and difluoroboron series on optical absorption and fluorescence emission properties have been made. Weaker electron donor–acceptor (D–A) pairs in both the oxazinone and quinazoline series bring about the slight red shifts of absorption spectra, whereas they significantly promote the fluorescence intensities of the oxazinone series but bathochromically shift the maximum emission wavelengths of the quinazoline series. Intrinsically, the charge-transfer (CT) modes govern the electron excitation/de-excitation processes in both the oxazinone and quinazoline series, but with respective different CT features, i.e., the interfragment CT mode for the oxazinone series versus the intrafragment CT mode for the quinazoline series. In the difluoroboron series, Oxa-Cl-OCH3-BF2 undergoes a change of transition mode from the local excitation to the CT de-excitation, whereas a large variation of CT compositions can be observed in Qui-Cl-OCH3-BF2. Experimentally, Oxa-Cl-OCH3-BF2 exhibits higher fluorescence quantum yield, favorable thermo- and photostability, stronger fluorescence intensity, and appropriately large Stokes shift, whereas theoretically, Qui-Cl-OCH3-BF2 benefiting from both the difluoroboron and quinazoline moieties is also promising to be a good fluorescent dye. The motif of combining oxazinone/quinazoline and difluoroboron moieties is believed to improve the prototypical architectures of oxazinone and quinazoline dyes.

# Highly Stable, Water-Soluble, Intrinsic Fluorescent Hybrid Scaffolds for Imaging and Biosensing\_2011

Nanoscale metal–organic particles (NMOPs) are constructed from metal ions and organic bridging ligands via the self-assembly process. Herein, we fabricate NMOPs composed of Mn2+ and a near-infrared (NIR) dye, IR825, obtaining Mn-IR825 NMOPs, which are then coated with a shell of polydopamine (PDA) and further functionalized with polyethylene glycol (PEG). While Mn2+ in such Mn-IR825@PDA–PEG NMOPs offers strong contrast in T1-weighted magnetic resonance (MR) imaging, IR825 with strong NIR optical absorbance shows efficient photothermal conversion with great photostability in the NMOP structure. Upon intravenous injection, Mn-IR825@PDA–PEG shows efficient tumor homing together with rapid renal excretion behaviors, as revealed by MR imaging and confirmed by biodistribution measurement. Notably, when irradiated with an 808 nm laser, tumors on mice with Mn-IR825@PDA–PEG injection are completely eliminated without recurrence within 60 days, demonstrating the high efficacy of photothermal therapy with this agent. This study demonstrates the use of NMOPs as a potential photothermal agent, which features excellent tumor-targeted imaging and therapeutic functions, together with rapid renal excretion behavior, the latter of which would be particularly important for future clinical translation of nanomedicine.

# Insights into the Photobehavior of Fluorescent Oxazinone, Quinazoline, and Difluoroboron Derivatives: Molecular Design Based on the Structure–Property Relationships\_2017

The photophysical, photochemical, two-photon absorption (2PA) and metal ion sensing properties of a new fluorene derivative (E)-1-(7-(4-(benzo[d]thiazol-2-yl)styryl)-9,9-bis(2-(2-ethoxyethoxy)ethyl)-9H-fluoren-2-yl)-3-(2-(9,10,16,17,18,19,21,22,23,24-decahydro-6H dibenzo[h,s][1,4,7,11,14,17]trioxatriazacycloicosin-20(7H)-yl)ethyl)thiourea (1) were investigated in organic and aqueous media. High sensitivity and selectivity of 1 to Zn2+ in tetrahydrofuran and a water/acetonitrile mixture were shown by both absorption and fluorescence titration. The observed complexation processes corresponded to 1:1 stoichiometry with the range of binding constants ∼(2−3) × 105 M−1. The degenerate 2PA spectra of 1 and 1/Zn2+ complex were obtained in the 640−900 nm spectral range with the maximum values of two-photon action cross section for ligand/metal complex ∼(90−130) GM, using a standard two-photon induced fluorescence methodology under femtosecond excitation. The nature of the 2PA bands was analyzed by quantum chemical methods and a specific dependence on metal ion binding processes was shown. Ratiometric fluorescence detection (420/650 nm) provided a good dynamic range (10−4 to 10−6 M) for detecting Zn2+, which along with the good photostability and 2PA properties of probe 1 makes it a good candidate in two-photon fluorescence microscopy imaging and sensing of Zn ions.

# Nanoscale Metal–Organic Particles with Rapid Clearance for Magnetic Resonance Imaging-Guided Photothermal Therapy\_2016

The design of a safe and sustainable process for the synthesis of hydrogen peroxide (H2O2) is a very important subject from the viewpoint of green chemistry. Photocatalytic H2O2 production with earth-abundant water and molecular oxygen (O2) as resources is an ideal process. A successful system based on an organic semiconductor has been proposed; however, it suffers from poor photostability. Here we report an inorganic photocatalyst for H2O2 synthesis. Visible light irradiation (λ >420 nm) of the semiconductor BiVO4 loaded with Au nanoparticles (Au/BiVO4) in pure water with O2 successfully produces H2O2. The bottom of the BiVO4 conduction band (0.02 V vs NHE, pH 0) is more positive than the one-electron reduction potential of O2 (−0.13 V) while more negative than the two-electron reduction potential of O2 (0.68 V). This thus suppresses one-electron reduction of O2 and selectively promotes two-electron reduction of O2, resulting in efficient H2O2 formation.

# Fluorene-Based Metal-Ion Sensing Probe with High Sensitivity to Zn2+ and Efficient Two-Photon Absorption\_2010

We introduce a new technique to measure tracer dynamics, which is sensitive to single metal nanoparticles down to a radius of 2.5 nm with a time resolution of a few microseconds. It is based on a fluctuation analysis of a heterodyne photothermal scattering signal emanating from the hot halo around the laser-heated tracer. A generalized Stokes−Einstein relation for “hot Brownian motion” is developed and verified. Exploiting the excellent photostability of gold nanoparticles, the developed method promises broad applications especially in the field of quantitative biomedical screening.

# Au Nanoparticles Supported on BiVO4: Effective Inorganic Photocatalysts for H2O2 Production from Water and O2 under Visible Light\_2016

Herein a green synthetic route has been developed for the synthesis of water-soluble CQDs by facile single-step hydrothermal treatment of latexes of E. milii plant for the first time. This methodology is zero-cost; uses ultrapure water as a green solvent; does not use strong concentrated acid; and avoids the use of post surface passivating agents. The as-prepared CQDs exhibited excellent optical properties, including high QY up to 39.2%, resistance to high salt strength, and long time photostability. Furthermore, the as-prepared CQDs served as an intrinsic peroxidase-mimic activity to catalyze the chromogenic substrate 3,3′,5,5′-tetramethylbenzidine (TMB) associated with H2O2, which resulted into a blue-colored reaction with a characteristic absorbance peak at 652 nm. Afterward, the proposed TMB-based oxidation system act as a probe for the detection of GSH and offers the high selectivity relative to the different amino acids and various other interfering agents which can be easily seen with naked eye. The limit of detection (LOD) was found to be 5.3 nM in a linear range 0.02 to 0.1 μM of GSH concentration which showed to be superior under the optimal condition as compared with another probe. To demonstrate the practical feasibility for the GSH detection, the present system was successfully applied on human blood serums with good recovery.

# Hot Brownian Particles and Photothermal Correlation Spectroscopy\_2009

We developed a simple non-hot-injection synthetic route that achieves in situ halide-passivated PbS and PbSe quantum dots (QDs) and simplifies the fabrication of Pb-chalcogenide QD solar cells. The synthesis mechanism follows a temperature-dependent diffusion growth model leading to strategies that can achieve narrow size distributions for a range of sizes. We show that PbS QDs can be produced with a diameter as small as 2.2 nm, corresponding to a 1.7 eV band gap, while the resulting size distribution (6–7%) is comparable to that of hot-injection syntheses. The in situ chloride surface passivation is demonstrated by X-ray photoelectron spectroscopy and an improved photostability of both PbS and PbSe QDs when stored under air. Additionally, the photoluminescence quantum yield of the PbS QDs is ∼30% higher compared to the traditional synthesis. We show that PbS QD solar cells with 6.5% power conversion efficiency (PCE) can be constructed. Finally, we fabricated PbSe QD solar cells in air (rather than in inert atmosphere), achieving a PCE of 2.65% using relatively large QDs with a corresponding band gap of 0.89 eV.

# A Facile and Simple Strategy for the Synthesis of Label Free Carbon Quantum Dots from the latex of Euphorbia milii and Its Peroxidase-Mimic Activity for the Naked Eye Detection of Glutathione in a Human Blood Serum\_2018

The orientations of both a nematic liquid crystal fluid and a series of monodisperse glassy−nematic oligofluorenes were investigated on photoalignment films comprising a polymethacrylate backbone with 7-benzoyloxycoumarin pendants. Both classes of liquid crystalline material were found to undergo a transition from a parallel to a perpendicular orientation with reference to the polarization axis of UV-irradiation at a sufficiently high extent of dimerization. The UV−vis and FTIR spectroscopic analyses revealed photostability with irradiation up to a fluence of 10 J/cm2, thereby excluding photodegradation as the basis for the observed crossover. A kinetic model was used to interpret the crossover behavior for irradiation at 25 °C, leading to the conclusion that liquid crystal molecules interact more favorably with coumarin monomers than with dimers. Through thermal annealing above Tg followed by cooling to room temperature, a glassy−nematic pentafluorene film was prepared on a photoalignment film, exhibiting an orientational order parameter comparable to that on a rubbed polyimide film. At an increasing oligofluorene chain length, however, a decreasing orientational order parameter emerged, presumably because of the increased annealing temperature that causes an orientational relaxation on the part of the dimerized coumarin moieties.

# Diffusion-Controlled Synthesis of PbS and PbSe Quantum Dots with in Situ Halide Passivation for Quantum Dot Solar Cells\_2013

We examine the use of thionylphosphazene-based block copolymers as matrixes for oxygen sensor applications. Poly(aminothionylphosphazene)-b-poly(tetrahydrofuran) (PATPy−PTHFx) block copolymers were prepared via reaction of ring-opened poly(chlorothionylphosphazene) with THF and subsequently with excess n-butylamine (to form PBATPy−PTHFx) or methylamine (to form PMATPy−PTHFx). The block copolymers were characterized by NMR, gel permeation chromatography, and differential scanning calorimetry. Films of PBATPy−PTHFx block copolymers containing platinum octaethylporphyrin or [Ru(dpp)3]Cl2 (dpp = 4,7-diphenyl-1,10-phenanthroline) as the oxygen-sensitive chromophore were prepared, and time-scan experiments were carried out to determine the diffusion coefficients, DO2, and solubilities, SO2, of oxygen therein. Despite microphase separation, the data fit well to a simple Fick's law description of oxygen diffusion and gave DO2 values smaller than that for the n-butylamino-substituted PBATP635. For films freshly annealed above the melting point of PTHFx, the DO2values were 35−50% (dye-dependent) larger than after aging 3 days at room temperature. Films with [Ru(dpp)3]Cl2 as the dye were evaluated as media for phosphorescent pressure-sensing. The dye-containing polymer films exhibit linear Stern−Volmer-like plots, even at high dye concentrations, as well as good photostability, and significantly higher sensitivity to oxygen quenching than simple mixtures of the analogous homopolymers.

# Photoalignment of a Nematic Liquid Crystal Fluid and Glassy−Nematic Oligofluorenes on Coumarin-Containing Polymer Films\_2006

The sulfonated phenylenevinylene polyanion derivate (APPV) and exfoliated Mg−Al-layered double hydroxide (LDH) monolayers were alternatively assembled into ordered ultrathin films (UTFs) employing a layer-by-layer method, which shows uniform yellow luminescence. UV−vis absorption and fluorescence spectroscopy present a stepwise and regular growth of the UTFs upon increasing deposited cycles. X-ray diffraction, atomic force microscopy, and scanning electron microscopy demonstrate that the UTFs are orderly periodical layered structure with a thickness of 3.3−3.5 nm per bilayer. The APPV/LDH UTFs exhibit well-defined polarized photoemission characteristic with the maximum luminescence anisotropy of ∼0.3. Moreover, the UTF exhibit longer fluorescence lifetime (3−3.85-fold) and higher photostability than the drop-casting APPV film under UV irradiation, suggesting that the existence of a LDH monolayer enhances the optical performance of the APPV polyanion. A combination study of electrochemistry and periodic density functional theory was used to investigate the electronic structure of the APPV/LDH system, illustrating that the APPV/LDH UTF is a kind of organic−inorganic hybrid multiple quantum well (MQW) structure with a low band energy of 1.7−1.8 eV, where the valence electrons of APPV can be confined into the energy wells formed by the LDH monolayers effectively. Therefore, this work not only gives a feasible method for fabricating a luminescence ultrathin film but also provides a detailed understanding of the geometric and electronic structures of photoactive polyanions confined between the LDH monolayers.

# Phosphorescent Oxygen Sensors Utilizing Sulfur−Nitrogen−Phosphorus Polymer Matrixes:  Synthesis, Characterization, and Evaluation of Poly(thionylphosphazene)-b-Poly(tetrahydrofuran) Block Copolymers\_2000

With increased interest in semiconductor nanoparticles for use in quantum dot solar cells there comes a need to understand the long-term photostability of such materials. Colloidal CdSe quantum dots (QDs) were suspended in toluene and stored in combinations of light/dark and N2/O2 to simulate four possible benchtop storage environments. CdSe QDs stored in a dark, oxygen-free environment were observed to better retain their optical properties over the course of 90 days. The excited state lifetimes, determined through femtosecond transient absorption spectroscopy, of air-equilibrated samples exposed to light exhibit a decrease in average lifetime (0.81 ns) when compared to samples stored in a nitrogen/dark environment (8.3 ns). A photoetching technique commonly used for controlled reduction of QD size was found to induce energetic trap states to CdSe QDs and accelerate the rate of electron–hole recombination. X-ray absorption near edge structure (XANES) analysis confirms surface oxidation, the extent of which is shown to be dependent on the thickness of the ligand shell.

# Anionic Poly(p-Phenylenevinylene)/Layered Double Hydroxide Ordered Ultrathin Films with Multiple Quantum Well Structure: A Combined Experimental and Theoretical Study\_2010

We report studies on several methylated uracils and thymines and thymine−water complexes in the gas phase using resonantly enhanced multiphoton ionization (REMPI) and laser-induced fluorescence (LIF) spectroscopy. Results from two different REMPI experiments provided strong evidence that, after photoexcitation to the S1 state, bare molecules were funneled into and trapped in a dark state via fast internal conversion. Lifetimes of this dark state were determined to be tens to hundreds of nanoseconds, depending on the internal energy and the degree of methyl substitution. The mass spectra of hydrated thymine clusters demonstrated dependence on the excitation wavelength, and the gradual loss of the ion signal with increasing water content across the absorption region of the S1 state indicated a reduced lifetime of the S1 state by the water solvent. In addition, the lifetime of the dark state also decreased gradually as thymine became more hydrated. On the basis of these results, we conclude that, in water solutions, the decay from the S1 state should be essentially fast internal conversion to the ground state, in agreement with studies from the liquid phase. Our work reveals that the photostability is not an intrinsic property of these pyrimidine bases. Rather, it is the water solvent that stabilizes the photophysical and photochemical behavior of these bases under UV irradiation.

# Photoinduced Surface Oxidation and Its Effect on the Exciton Dynamics of CdSe Quantum Dots\_2012

A fluorescence sensing material based on quantum dots with excellent optical properties and molecularly imprinted polymer (QDs@MIP) with specific recognition has been developed. First the surface of CdSe/ZnS QDs was modified with ionic liquids (ILs) by electrostatic interaction. The fluorescence sensing material was constructed from anchoring the MIP layer on IL modified CdSe/ZnS QDs by copolymerization, which had been developed for the detection of carbaryl in rice and Chinese cabbage. The MIP fluorescence was more strongly quenched by carbaryl than the non-imprinted polymer (NIP) fluorescence, which indicated that the QDs@MIP could selectively recognize the corresponding carbaryl. Furthermore, the developed QDs@MIP method was validated by HPLC and ELISA respectively, and the results of these methods were well correlated (R2 = 0.98). The fluorescence sensing material had obvious advantages, such as being easily prepared and having specific recognition and photostability. The developed method was simple and effective for the detection of carbaryl. And, it could also provide the technical support for the rapid detection in food safety fields.

# Photophysics of Methyl-Substituted Uracils and Thymines and Their Water Complexes in the Gas Phase\_2004

With increased interest in semiconductor nanoparticles for use in quantum dot solar cells there comes a need to understand the long-term photostability of such materials. Colloidal CdSe quantum dots (QDs) were suspended in toluene and stored in combinations of light/dark and N2/O2 to simulate four possible benchtop storage environments. CdSe QDs stored in a dark, oxygen-free environment were observed to better retain their optical properties over the course of 90 days. The excited state lifetimes, determined through femtosecond transient absorption spectroscopy, of air-equilibrated samples exposed to light exhibit a decrease in average lifetime (0.81 ns) when compared to samples stored in a nitrogen/dark environment (8.3 ns). A photoetching technique commonly used for controlled reduction of QD size was found to induce energetic trap states to CdSe QDs and accelerate the rate of electron–hole recombination. X-ray absorption near edge structure (XANES) analysis confirms surface oxidation, the extent of which is shown to be dependent on the thickness of the ligand shell.

# In Situ Live-Cell Nucleus Fluorescence Labeling with Bioinspired Fluorescent Probes\_2017

Porous silicon (PSi) has attracted wide interest as a potential material for various fields of nanomedicine. However, until now, the application of PSi in photothermal therapy has not been successful due to its low photothermal conversion efficiency. In the present study, biodegradable black PSi (BPSi) nanoparticles were designed and prepared via a high-yield and simple reaction. The PSi nanoparticles possessed a low band gap of 1.34 eV, a high extinction coefficient of 13.2 L/g/cm at 808 nm, a high photothermal conversion efficiency of 33.6%, good photostability, and a large surface area. The nanoparticles had not only excellent photothermal properties surpassing most of the present inorganic photothermal conversion agents (PCAs) but they also displayed good biodegradability, a common problem encountered with the inorganic PCAs. The functionality of the BPSi nanoparticles in photothermal therapy was verified in tumor-bearing mice in vivo. These results showed clearly that the photothermal treatment was highly efficient to inhibit tumor growth. The designed PCA material of BPSi is robust, easy to prepare, biocompatible, and therapeutically extremely efficient and it can be integrated with several other functionalities on the basis of simple silicon chemistry.

# Scalable Synthesis of Biodegradable Black Mesoporous Silicon Nanoparticles for Highly Efficient Photothermal Therapy\_2018

In this work, the effects of α-linolenic acid (ALA) loaded in oil-in-water (O/W) and water-in-oil-in-water (W/O/W) microemulsions on cell viability, lactic dehydrogenase (LDH) viability, and reactive oxygen species (ROS) levels were examined using Cell Counting Kit-8 (CCK-8), an LDH assay kit, and a fluorescence microscope, respectively. The CCK-8 assay demonstrated that ALA inhibited MDA-MB-231 human breast cancer cell proliferation in a dose-dependent manner. Further, the results of LDH activity and ROS levels revealed that ALA-induced cancer cell damage was closely related to oxidative stress. Under the irradiation of ultraviolet light, the microemulsion without any added fluorescent dye would emit bright blue fluorescence, and the fluorescent images of the cells treated with ALA-loaded O/W and W/O/W microemulsions at different incubation times were taken, which exhibited long-term photostability and biocompatibility. In addition, the fluorescence mechanism of the microemulsion was explained by immobilizing surfactant molecules with aggregation-induced emission (AIE) properties at the water–oil interface through the microemulsion with a self-assembled structure. These findings showed the potential application of O/W and W/O/W microemulsions as the label-free delivery carriers in long-term imaging of living cells and real-time release monitoring of nutrients.

# Development of Fluorescence Sensing Material Based on CdSe/ZnS Quantum Dots and Molecularly Imprinted Polymer for the Detection of Carbaryl in Rice and Chinese Cabbage\_2015

Fluorescent systems that can undergo intensity photomodulation in aqueous environments are finding increasing applications, particularly in high-resolution imaging of biological samples. We seek to develop conjugated polymer nanoparticles (CPNs) with bright fluorescence that can be modulated with a light signal. Here, we present CPNs, doped with a photochromic diarylethene dye, that exhibit efficient fluorescence photomodulation that is thermally irreversible. In their UV-absorbing open form, the diarylethenes have no effect on the fluorescence properties of the bright CPNs. A brief period of UV irradiation converts the dyes to their visible-absorbing closed form, which is an efficient fluorescence quencher for the CPNs, likely via a fluorescence resonance energy transfer mechanism. Aqueous suspensions of dye-doped CPNs prepared from the homopolymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) or a polyfluorene-phenylenevinylene copolymer (PFPV) exhibit thermally stable bright and dark levels. The dye-doped MEH-PPV CPNs also exhibit photomodulation in single-nanoparticle imaging experiments, which reveal that nearly all CPNs retain a small amount of residual emission in the dark state. Their PFPV counterparts undergo irreversible fluorescence photobleaching rather than photomodulation in single-nanoparticle studies. The photostability of the CPNs under the UV irradiation conditions required for photochromic conversion is investigated on the single-particle level, and PFPV CPNs are found to be particularly susceptible to photobleaching upon 254 nm irradiation. These results will guide the selection of polymers and photochromes for CPNs intended for single-particle photomodulation.

# Antiproliferative Ability and Fluorescence Tracking of α-Linolenic Acid-Loaded Microemulsion as Label-Free Delivery Carriers in MDA-MB-231 Cells\_2019

Metallic nanostructures as excellent candidates for nanosensitizers have shown enormous potentials in cancer radiotherapy and photothermal therapy. Clinically, a relatively low and safe radiation dose is highly desired to avoid damage to normal tissues. Therefore, the synergistic effect of the low-dosed X-ray radiation and other therapeutic approaches (or so-called “combined therapeutic strategy”) is needed. Herein, we have synthesized hollow and spike-like gold nanostructures by a facile galvanic replacement reaction. Such gold nanospikes (GNSs) with low cytotoxicity exhibited high photothermal conversion efficiency (η = 50.3%) and had excellent photostability under cyclic near-infrared (NIR) laser irradiations. We have demonstrated that these GNSs can be successfully used for in vitro and in vivo X-ray radiation therapy and NIR photothermal therapy. For the in vitro study, colony formation assay clearly demonstrated that GNS-mediated photothermal therapy and X-ray radiotherapy reduced the cell survival fraction to 89% and 51%, respectively. In contrast, the cell survival fraction of the combined radio- and photothermal treatment decreased to 33%. The synergistic cancer treatment performance was attributable to the effect of hyperthermia, which efficiently enhanced the radiosensitizing effect of hypoxic cancer cells that were resistant to ionizing radiation. The sensitization enhancement ratio (SER) of GNSs alone was calculated to be about 1.38, which increased to 1.63 when the GNS treatment was combined with the NIR irradiation, confirming that GNSs are effective radiation sensitizers to enhance X-ray radiation effect through hyperpyrexia. In vivo tumor growth study indicated that the tumor growth inhibition (TGI) in the synergistically treated group reached 92.2%, which was much higher than that of the group treated with the GNS-enhanced X-ray radiation (TGI = 29.8%) or the group treated with the GNS-mediated photothermal therapy (TGI = 70.5%). This research provides a new method to employ GNSs as multifunctional nanosensitizers for synergistic NIR photothermal and X-ray radiation therapy in vitro and in vivo.

# Ensemble and Single-Particle Fluorescence Photomodulation in Diarylethene-Doped Conjugated Polymer Nanoparticles\_2011

Spectroscopically resolved emission from single nanocrystals at cryogenic temperatures provides unique insight into physical processes that occur within these materials. At low temperatures, the emission spectra collapse to narrow lines, revealing a rich spectroscopic landscape and unexpected properties, completely hidden at the ensemble level. Since these techniques were first used, the technology of nanocrystal synthesis has matured significantly, and new materials with outstanding photostability have been reported. In this perspective, we show how cryogenic spectroscopy of single nanocrystals probes the fundamental excitonic structure of the band edge, revealing spectral fingerprints that are highly sensitive to a range of photophysical properties as well as nanocrystal morphology. In particular, spectral and temporal signatures of biexciton and trion emission are revealed, and their relevance to emerging technologies is discussed. Overall we show how cryogenic single nanocrystal spectroscopy can be used as a tool for understanding fundamental photophysics and guiding the synthesis of new nanocrystal materials.

# Enhanced Radiosensitization of Gold Nanospikes via Hyperthermia in Combined Cancer Radiation and Photothermal Therapy\_2016

Molecular photosensitizers play a key role in many areas of renewable-energy chemistry and technology, including dye-sensitized solar cells and photocatalysis reactions that generate small-molecule fuels. Although there is much research effort that uses existing “off-the-shelf” photosensitizers to optimize these processes, it is also important to continue to develop new and improved photosensitizers, which can also lead to advances in photovoltaic and photocatalysis applications. Moving beyond the ubiquitous ruthenium polypyridyl class of photosensitizers, recent research has shown that complexes of other transition metals can have improved attributes, in particular, with regard to photostability and excited-state redox properties. In this Perspective, we highlight recent advances in photosensitizer design. We begin with a tutorial on the important criteria for photosensitizer design, following which we describe recent advances and expected future directions that demonstrate the ability to use synthetic chemistry to optimize the excited-state attributes of photosensitizer molecules.

# Cryogenic Single-Nanocrystal Spectroscopy: Reading the Spectral Fingerprint of Individual CdSe Quantum Dots\_2013

Fluorescence nanoscopy provides means to discern the finer details of protein localization and interaction in cells by offering an order of magnitude higher resolution than conventional optical imaging techniques. However, these super resolution techniques put higher demands on the optical system and the fluorescent probes, making multicolor fluorescence nanoscopy a challenging task. Here we present a new and simple procedure, which exploits the photostability and excitation spectra of dyes to increase the number of simultaneous recordable targets in STED nanoscopy. We use this procedure to demonstrate four-color STED imaging of platelets with ≤40 nm resolution and low crosstalk. Platelets can selectively store, sequester, and release a multitude of different proteins, in a manner specific for different physiological and disease states. By applying multicolor nanoscopy to study platelets, we can achieve spatial mapping of the protein organization with a high resolution for multiple proteins at the same time and in the same cell. This provides a means to identify specific platelet activation states for diagnostic purposes and to understand the underlying protein storage and release mechanisms. We studied the organization of the pro- and antiangiogenic proteins VEGF and PF-4, together with fibrinogen and filamentous actin, and found distinct features in their respective protein localization. Further, colocalization analysis revealed only minor overlap between the proteins VEGF and PF-4 indicating that they have separate storage and release mechanisms, corresponding well with their opposite roles as pro- and antiangiogenic proteins, respectively.

# Molecular Photosensitizers in Energy Research and Catalysis: Design Principles and Recent Developments\_2019

Noble-metal nanomaterials were widely investigated as theranostic systems for surface enhanced Raman scattering (SERS) imaging, and also for photothermal therapy (PTT) of cancers. However, it was still a major challenge to explore multifunctional nanoprobes with high performance, high stability, and low toxicity. In this work, Raman reporter (DTTC)-coupled Agcore@Aushell nanostars (Ag@Au-DTTC) were synthesized and investigated for in vivo improved SERS imaging and near-infrared (NIR)-triggered PTT of breast cancers. By the two-step coupling of DTTC, the SERS signal was improved obviously, and the cytotoxicity of nanoparticles was also decreased by coating Au nanostars onto Ag nanoparticles. The as-prepared Ag@Au-DTTC nanostars showed high photostability and excellent photothermal performance, in which the photothermal conversion efficiency was up to 79.01% under the irradiation of an 808 nm laser. The in vitro and in vivo SERS measurements of Ag@Au-DTTC nanostars showed that the many sharp and narrow Raman peaks located at 508, 782, 844, 1135, 1242, 1331, 1464, 1510, and 1580 cm–1 could be obviously observed in MCF-7 cells and in MCF-7 tumor-bearing nude mice, compared with that in pure DTTC. In 14-day treatments, the tumor volume of MCF-7 tumor-bearing nude mice injected with Ag@Au-DTTC nanostars and irradiated by an 808 nm laser almost disappeared. This study demonstrated that the as-prepared Ag@Au-DTTC nanostars could be excellent multifunctional agents for improved SERS imaging and NIR-triggered PTT of breast cancers with low risk.

# Multicolor Fluorescence Nanoscopy by Photobleaching: Concept, Verification, and Its Application To Resolve Selective Storage of Proteins in Platelets\_2014

Conspectus  
The modern history of conducting organic systems started with a fortuitous error in 1967 on acetylene polymerization, followed by a rational discovery in 1976 on the effects of doping that generates a polaron and, hence, dramatically increases conductivity. Not unexpectedly, however, the prototypical polyacetylene suffers many problems, including C–C single bond rotation, short effective conjugation length, radiationless deactivation, and instability of the polarons. Several strategies have been put in place to solve these problems. An early approach relied on partial rigidification of the polyene structure by conversion into polymers with thiophene, pyrrole, and benzene linkages. An oligo(phenylene vinylene) (OPV) is an all-carbon analogue of polyacetylene, where every other diene unit in the polyene chain is converted to a benzene unit, still leaving many C–C single bonds freely rotating in the molecule. We considered adding additional carbon bridges to rigidify the OPV skeleton entirely to create a carbon-bridged OPV (COPV).  
Making such a compound was an obvious challenge. This Account describes the authors’ efforts to design and synthesize a series of COPV molecules, where the benzene rings in OPV are bridged by sp3 carbon atoms to form a bicyclo[3.3.0]octatriene framework bearing a tetrasubstituted olefin at the ring fusion. This olefinic bond is so strained that it resists further deformation or conversion to sp3 centers, and hence, it is chemically stable despite the strain. The sp3 carbon bridges can bear organic side chains that hinder intermolecular interactions, rendering the excited states stable and long-lived even in the solid state. They also increase solubility, a common problem among rigid molecular systems. With these structural features, the COPV molecules were found to be well behaved both at a single-molecule level and as a bulk material. We reported in 2009 a method for the synthesis of COPVs and have, since then, reported their structures and physicochemical properties, including basic photophysical properties of neutral and charged derivatives, thermal and photostability, and fast electron transfer. These properties have rendered the COPV molecules useful for electronic and photonic research, for example, lasers, solar cells, and molecular wire applications.  
Noteworthy discoveries in the area connecting chemistry and physics include inelastic tunneling and long-range resonance tunneling at ambient temperature, which were previously observed only for organic molecular wires placed under cryogenic conditions. Given the ready availability of the COPV skeleton bearing a wide variety of substituents, this class of molecules will serve as versatile building blocks for fundamental and applied research on physicochemical and materials chemistry.

# Raman Reporter-Coupled Agcore@Aushell Nanostars for in Vivo Improved Surface Enhanced Raman Scattering Imaging and Near-infrared-Triggered Photothermal Therapy in Breast Cancers\_2015

Leucine aminopeptidase (LAP), one of the important proteolytic enzymes, is intertwined with the progress of many pathological disorders as a well-defined biomarker. To explore fluorescent aminopeptidase probe for quantitative detection of LAP distribution and dynamic changes, herein we report a LAP-targeting near-infrared (NIR) fluorescent probe (DCM–Leu) for ratiometric quantitative trapping of LAP activity in different kinds of living cells. DCM–Leu is composed of a NIR-emitting fluorophore (DCM) as a reporter and l-leucine as a triggered moiety, which are linked together by an amide bond specific for LAP cleavage. High contrast on the ratiometric NIR fluorescence signal can be achieved in response to LAP activity, thus enabling quantification of endogenous LAP with “build-in calibration” as well as minimal background interference. Its ratiometric NIR signal can be blocked in a dose-dependent manner by bestatin, an LAP inhibitor, indicating that the alteration of endogenous LAP activity results in these obviously fluorescent signal responses. It is worth noting that DCM–Leu features striking characteristics such as a large Stokes shift (∼205 nm), superior selectivity, and strong photostability responding to LAP. Impressively, not only did we successfully exemplify DCM–Leu in situ ratiometric trapping and quantification of endogenous LAP activity in various types of living cells, but also, with the aid of three-dimensional confocal imaging, the intracellular LAP distribution is clearly observed from different perspectives for the first time, owing to the high signal-to-noise of ratiometric NIR fluorescent response. Collectively, these results demonstrate preclinical potential value of DCM–Leu serving as a useful NIR fluorescent probe for early detection of LAP-associated disease and screening inhibitor.

# Carbon-Bridged Oligo(phenylene vinylene)s: A de Novo Designed, Flat, Rigid, and Stable π-Conjugated System\_2019

Development of luminescence probes with polarized and narrow emissions simultaneously is helpful for removing multiply scattered light and enables multiplexing detection, but it remains challenging to use conventional organic dyes, fluorescence proteins, and quantum dots. Here, we demonstrated smart one-dimensional microlaser probes (MLPs) by coating a thin layer of silica shell on the surface of organic nanowires (ONWs) of 1,4-dimethoxy-2,5-di[4′-(methylthio)styryl]benzene (TDSB), namely, ONW@SiO2 core–shell structures. Different from the Fabry–Pérot (FP) cavity formed between two end-faces of semiconductor nanowires, whispering gallery mode (WGM) microresonators are built within the rectangular cross section of ONW@SiO2 MLPs. This enables a lasing threshold as low as 1.54 μJ/cm2, above which lasing emissions are obtained with a full width at half-maximum (fwhm) < 5 nm and a degree of polarization (DOP) > 83%. Meanwhile, small dimensions of ONW@SiO2 MLPs with a side-length of ca. 500 nm and a length of 3–8 μm help to reduce their perturbations in living cells. With the help of mesoporous silica shells, which provide both high biocompatibility and good photostability, ONW@SiO2 MLPs can be easily introduced into the cell cytoplasm through natural endocytosis. Using their narrow and highly polarized lasing emissions in vitro, we demonstrate that it is possible to tag individual cells using ONW@SiO2 MLPs with high stability.

# In Situ Ratiometric Quantitative Tracing of Intracellular Leucine Aminopeptidase Activity via an Activatable Near-Infrared Fluorescent Probe\_2016

Enzymes play an indispensable role in maintaining normal life activities. The abnormalities of content and activity in specific enzymes are usually associated with the occurrence and the development of major diseases. Correspondingly, fluorescent bioprobes with distinctive sensing mechanisms and different functionalities have attracted growing attention as convenient tools for optical probing and monitoring the activity of enzymes. Ideally and excitedly, the recently emerged luminogens with an aggregation-induced emission (AIE) feature could perfectly overcome the aggregation-caused quenching (ACQ) effect of conventional bioprobes. Based on the fantastic characteristics of AIE luminogens (AIEgens), specific enzyme bioprobes have been designed through integration with recognition units, demonstrating many advantages including low background interference, a high signal-to-noise ratio (SNR), and superior photostability. In this review, by presenting some typical examples, we summarize the working principle and structural design of specific AIEgen-based bioprobes that are triggered by enzymes and discuss their great potential in biomedical applications, with the aim to promote the future research of fluorescent bioprobes involving enzymes.

# Organic-Nanowire–SiO2 Core–Shell Microlasers with Highly Polarized and Narrow Emissions for Biological Imaging\_2017

Self-assembly is the basic feature of supramolecular chemistry, which permits to integrate and enhance the functionalities of nano-objects. However, the conversion of self-assembled structures to practical materials is still laborious. In this work, on the basis of studying one-pot synthesis, spontaneous assembly, and in situ polymerization of aqueous semiconductor nanocrystals (NCs), NC self-assembly materials are produced and applied to design high performance white light-emitting diode (WLED). In producing self-assembly materials, the additive hydrazine (N2H4) is curial, which acts as the promoter to achieve room-temperature synthesis of aqueous NCs by favoring a reaction-controlled growth, as the polyelectrolyte to weaken inter-NC electrostatic repulsion and therewith facilitate the one-dimensional self-assembly, and in particular as the bifunctional monomers to polymerize with mercapto carboxylic acid-modified NCs via in situ amidation reaction. This strategy is versatile for mercapto carboxylic acid-modified aqueous NCs, for example CdS, CdSe, CdTe, CdSexTe1–x, and CdyHg1–yTe. Because of the multisite modification with carboxyl, the NCs act as macromonomers, thus producing cross-linked self-assembly materials with excellent thermal, solvent, and photostability. The assembled NCs preserve strong luminescence and avoid unpredictable fluorescent resonance energy transfer, the main problem in design WLED from multiple NC components. These advantages allow the fabrication of NC-based WLED with high color rendering index (86), high luminous efficacy (41 lm/W), and controllable color temperature.

# Enzyme-Responsive Bioprobes Based on the Mechanism of Aggregation-Induced Emission\_2017

The sensitivity and resolution of single-molecule fluorescence imaging in biology are mainly limited by two known weaknesses of fluorescent proteins: label brightness and photostability. In this work, we use patterned gold substrates to achieve plasmon-enhanced emission from intrinsically fluorescent proteins in living pathogenic bacteria cells. By coupling membrane-bound single fluorescent protein fusions to the virulence regulator TcpP in living Vibrio cholerae bacteria to extracellular gold nanotriangle arrays, we use plasmonics to improve our measurements of this important question in pathogenesis: how does V. cholerae produce its deadly toxin? Based on a simple experimental geometry, we observe a 1.3× enhancement in the rate of emission and a 1.4× enhancement in the number of photons detected prior to photobleaching. Furthermore, by enhancing both the rate of emission and the total number of photons detected from single-molecule fluorescent probes in live cells, we show that plasmon-enhanced fluorescence is a biocompatible, generalizable path to directly improve the resolution and trajectory lengths of single molecules in live cells.

# Hydrazine-Mediated Construction of Nanocrystal Self-Assembly Materials\_2014

One of the most attractive commercial applications of semiconductor nanocrystals (NCs) is their use in lasers. Thanks to their high quantum yield, tunable optical properties, photostability, and wet-chemical processability, NCs have arisen as promising gain materials. Most of these applications, however, rely on incorporation of NCs in lasing cavities separately produced using sophisticated fabrication methods and often difficult to manipulate. Here, we present whispering gallery mode lasing in supraparticles (SPs) of self-assembled NCs. The SPs composed of NCs act as both lasing medium and cavity. Moreover, the synthesis of the SPs, based on an in-flow microfluidic device, allows precise control of the dimensions of the SPs, i.e. the size of the cavity, in the micrometer range with polydispersity as low as several percent. The SPs presented here show whispering gallery mode resonances with quality factors up to 320. Whispering gallery mode lasing is evidenced by a clear threshold behavior, coherent emission, and emission lifetime shortening due to the stimulation process.

# Plasmon-Enhanced Fluorescence from Single Proteins in Living Bacteria\_2015

Fluorescent semiconductor nanoplatelets (NPLs) are a new generation of fluorescent probes. NPLs are colloidal two-dimensional materials that exhibit several unique optical properties, including high brightness, photostability, and extinction coefficients, as well as broad excitation and narrow emission spectra from the visible to the near-infrared spectrum. All of these exceptional fluorescence properties make NPLs interesting nanomaterials for biological applications. However, NPLs are synthesized in organic solvents and coated with hydrophobic ligands that render them insoluble in water. A current challenge is to stabilize NPLs in aqueous media compatible with biological environments. In this work, we describe a novel method to disperse fluorescent NPLs in water and functionalize them with different biomolecules for biodetection. We demonstrate that ligand exchange enables the dispersion of NPLs in water while maintaining optical properties and long-term colloidal stability in biological environments. Four different colors of NPLs were functionalized with biomolecules by random or oriented conformations. For the first time, we report that our NPLs have a higher brightness than that of standard fluorophores, like phycoerythrin or Brilliant Violet 650 (BV 650), for staining cells in flow cytometry. These results suggest that NPLs are an interesting alternative to common fluorophores for flow cytometry and imaging applications in multiplexed cellular targeting.

# Lasing Supraparticles Self-Assembled from Nanocrystals\_2018

Discovery of an efficient catalyst bearing low overpotential toward water oxidation is a key step for light-driven water splitting into dioxygen and dihydrogen. A mononuclear ruthenium complex, Ru(II)L(pic)2 (1) (H2L = 2,2′-bipyridine-6,6′-dicarboxylic acid; pic = 4-picoline), was found capable of oxidizing water eletrochemically at a relatively low potential and promoting light-driven water oxidation using a three-component system composed of a photosensitizer, sacrificial electron acceptor, and complex 1. The detailed electrochemical properties of 1 were studied, and the onset potentials of the electrochemically catalytic curves in pH 7.0 and pH 1.0 solutions are 1.0 and 1.5 V, respectively. The low catalytic potential of 1 under neutral conditions allows the use of [Ru(bpy)3]2+ and even [Ru(dmbpy)3]2+ as a photosensitizer for photochemical water oxidation. Two different sacrificial electron acceptors, [Co(NH3)5Cl]Cl2 and Na2S2O8, were used to generate the oxidized state of ruthenium tris(2,2′-bipyridyl) photosensitizers. In addition, a two-hour photolysis of 1 in a pH 7.0 phosphate buffer did not lead to obvious degradation, indicating the good photostability of our catalyst. However, under conditions of light-driven water oxidation, the catalyst deactivates quickly. In both solution and the solid state under aerobic conditions, complex 1 gradually decomposed via oxidative degradation of its ligands, and two of the decomposed products, sp3 C−H bond oxidized Ru complexes, were identified. The capability of oxidizing the sp3 C−H bond implies the presence of a highly oxidizing Ru species, which might also cause the final degradation of the catalyst.

# Semiconductor Nanoplatelets: A New Class of Ultrabright Fluorescent Probes for Cytometric and Imaging Applications\_2018

A novel cuprous(I) cluster Cu4I4L4 (L = (E)-(4-diethylanilino-styryl)pyridine) bearing strong two-photon absorption (TPA) was obtained using a facile assembly method, and the crystal structure has been determined. Quantum chemical calculations using time-dependent density functional theory (TD-DFT) reveals that the combination of the organic ligands with the three-dimensional Cu4I4 core extends the electronic delocalization in the cluster, leading to strong two-photon absorption action. The TPA cross sections (Φσ2) of Cu4I4L4 were enhanced with increasing polarity of solvents, which is quite different from the solvent effects on TPA in the literature. Compared to its free ligand, the cluster Cu4I4L4 exhibits larger peak TPA cross sections in the near-infrared region, longer fluorescence lifetimes, higher quantum yield and photostability, lower cytotoxicity, and brighter two-photon fluorescent (TPF) bioimaging. These integrated advantages make it desirable to be applied as a two-photon fluorescent probe for labeling the nucleic acids in live cells.

# Visible Light-Driven Water Oxidation by a Molecular Ruthenium Catalyst in Homogeneous System\_2009

The photo-Fries rearrangement which was first reported (1,2) in the early 1960's has some potential in the design of photoresist materials since it involves the transformation of molecules such as phenolic esters into free phenols, thereby providing a route to selective image development by differential dissolution. Initial interest in the photo-Fries rearrangement of aromatic polyesters was mainly due to the fact the reaction is accompanied by the formation of o-hydroxy aromatic compounds which possess great photostability. This interesting property of the rearranged products can be used to design polymers containing photostabilizing ortho-hydroxy aromatic groups (3-6); the photostabilizing action of such compounds has been recently reviewed (7-8).  
Scheme 1 shows the reaction which occurs when an aromatic polyester such as [I] is subjected to UV irradiation (5). The polymer first undergoes main-chain cleavage with subsequent rearrangement to polymer [II] which is photostable and can be used as a thin coating to

# Assembly, Two-Photon Absorption, and Bioimaging of Living Cells of A Cuprous Cluster\_2011

Nanoshell and Matryoshka-nanoshell constructs are rationally optimized utilizing the finite-difference time-domain method to design probes with enhanced fluorescence. Through the systematical investigation of interactions between the spontaneous emission of a single emitter and a metal-based nanostructure, the plasmonic-enhanced fluorescence is found maximal for certain morphologies that balance two competitive factors: field enhancement and quantum efficiency. For instance, key parameters such as the emitter’s position, its orientation, and the spectral overlaps between molecular bands and plasmon resonance are investigated to fully understand the complete behavior of the system. In the case of metal nanoshells, it is shown that the molecular fluorescence is differently enhanced inside or outside the shell. In that of Matryoshka-nanoshells that consist of concentric gold core and shell, the construct appears as an exceptionally promising probe especially when the fluorophore lies within the gap layer. Indeed, the strong coupling between the adjacent core and shell allows electromagnetic excitation to be squeezed within the gap, so resulting in giant fluorescence and photostability. Such a construct opens a way for still increasing the sensitivity of fluorescence detection, which is promising for almost all biological imaging applications.

# Optimally Designed Nanoshell and Matryoshka-Nanoshell as a Plasmonic-Enhanced Fluorescence Probe\_2012

Protein aggregation is the hallmark of a number of neurodegenerative diseases including Parkinson’s and Huntington’s diseases. There is a significant interest in understanding the molecular mechanisms involved in the self-association and fibrillization of monomeric soluble proteins into insoluble deposits in vivo and in vitro. Probes with novel properties, such as red-shifted emission, large Stokes shifts, and high photostability, are desirable for a variety of protein aggregation studies. To respond to the increasing need for aggregation–responsive compounds suitable to cellular studies, we present a ruthenium(II) dipyridophenazine derivative, [Ru(phen)2dppz]2+ (phen =1,10-phenanthroline, dppz = dipyrido[3,2-a:2′.3′-c]phenazine), to study aggregation of α-synuclein (αS), which is associated with the development of Parkinson’s disease. We demonstrated the use of [Ru(phen)2dppz]2+ to monitor αS fibril formation in real-time and to detect and quantify αS aggregates in neuroglioma cells, thereby providing a novel molecular tool to study protein deposition diseases in vitro and in vivo.

# The Photo-Fries Rearrangement and Its Use in Polymeric Imaging Systems\_1985

Constructing semiconductor heterojunctions via surface/interface engineering is an effective way to enhance the charge carrier separation/transport ability and thus the photoelectrochemical (PEC) properties of a photoelectrode. Herein, we report a conformal BiVO4-layer/WO3-nanoplate-array heterojunction photoanode modified with cobalt phosphate (Co-Pi) as oxygen evolution cocatalyst (OEC) for significant enhancement in PEC performances. The BiVO4/WO3 nanocomposite is fabricated by coating a thin conformal BiVO4 layer on the surface of presynthesized WO3 nanoplate arrays (NPAs) via stepwise spin-coating, and the decoration of Co-Pi OEC is realized by photoassisted electrodeposition method. The optimized Co-Pi@BiVO4/WO3 heterojunction photoanode shows a maximum photocurrent of 1.8 mA/cm2 at 1.23 V vs RHE in a phosphate buffer electrolyte under an AM1.5G solar simulator, which is 5 and 12 times higher than those of bare WO3 and BiVO4 photoanode, respectively. Measurements of UV–vis absorption spectra, electrochemical impedance spectra (EIS) and photoluminescence (PL) spectra reveal that the enhanced PEC performances can be attributed to the increased charge carrier separation/transport benefited from the type II nature of BiVO4/WO3 heterojunction and the promoted water oxidation kinetics and photostability owing to the decoration of Co-Pi cocatalyst.

# Detection of α-Synuclein Amyloidogenic Aggregates in Vitro and in Cells using Light-Switching Dipyridophenazine Ruthenium(II) Complexes\_2012

Bifunctional nanocomposites with superparamagnetic and NIR luminescent properties were synthesized by a layer-by-layer and a modified Stöber method. Fe3O4 nanoparticles as the core were coated with NaYF4:Ln3+ (Ln = Nd, Er, Pr, or Ho) to form the first layer. Then, the second layer was coated with silica to improve the chemical stability and photostability. The X-ray diffraction patterns showed that a cubic spinel structure of Fe3O4 and the coexistence of a cubic and hexagonal structure of NaYF4 were obtained. Energy dispersive X-ray (EDX) spectroscopy analysis confirmed the core/shell structure of Fe3O4@NaYF4:Ln3+. Transmission electron microscopy images revealed that the bifunctional nanocomposites consisted of crystalline Fe3O4@NaYF4:Ln3+ cores and amorphous SiO2 shells, in a spherical shape with a narrow size distribution. Magnetic measurements showed that the obtained bifunctional nanocomposites exhibited superparamagnetic behavior. Emission spectra indicated that the bifunctional nanocomposites possessed a high near-infrared (NIR) luminescent intensity. Moreover, the hexagonal phase NaYF4:Ln3+ showed NIR emission 10 to 15 times stronger than the cubic phase.

# Conformal BiVO4-Layer/WO3-Nanoplate-Array Heterojunction Photoanode Modified with Cobalt Phosphate Cocatalyst for Significantly Enhanced Photoelectrochemical Performances\_2018

A simple, economical, and green method for the preparation of water-soluble, high-fluorescent carbon quantum dots (C-dots) has been developed via hydrothermal process using aloe as a carbon source. The synthesized C-dots were characterized by atomic force microscope (AFM), transmission electron microscopy (TEM), fluorescence spectrophotometer, UV–vis absorption spectra as well as Fourier transform infrared spectroscopy (FTIR). The results reveal that the as-prepared C-dots were spherical shape with an average diameter of 5 nm and emit bright yellow photoluminescence (PL) with a quantum yield of approximately 10.37%. The surface of the C-dots was rich in hydroxyl groups and presented various merits including high fluorescent quantum yield, excellent photostability, low toxicity and satisfactory solubility. Additionally, we found that one of the widely used synthetic food colorants, tartrazine, could result in a strong fluorescence quenching of the C-dots through a static quenching process. The decrease of fluorescence intensity made it possible to determine tartrazine in the linear range extending from 0.25 to 32.50 μM, This observation was further successfully applied for the determination of tartrazine in food samples collected from local markets, suggesting its great potential toward food routine analysis. Results from our study may shed light on the production of fluorescent and biocompatible nanocarbons due to our simple and environmental benign strategy to synthesize C-dots in which aloe was used as a carbon source.

# Preparation and Characterization of Near-Infrared Luminescent Bifunctional Core/Shell Nanocomposites\_2008

A pesticide's reactivity toward light at the leaf surface after crop treatment is rarely considered, although such degradation reactions directly affect the pesticide's effectiveness. To overcome these limitations, the use of plant pigments was proposed as a new class of photoprotecting agent. The photoprotecting properties of seven plant pigments were tested under controlled conditions over herbicide sulcotrione. Grape wine extracts were tested over a panel of pesticides from distinct chemical families. The addition of plant extracts almost systematically reduced the pesticide's photoreactivity. The grape wine extracts improve at least by 38% the half-life of photolysis of almost all of the active ingredients tested, except for the herbicide triclopyr. Fustictree extract increases by 82% the photostability of the herbicide sulcotrione. Plant extracts mainly act as sunscreens; that is, the photostabilization of the active ingredient is due to the competitive energy absorption of UV photon. The use of natural plant extracts is a promising strategy to limit pesticide photodegradation. It is a way to develop sustainable and innovative technology for the plant protection industry, being beneficial from both economic and ecological points of view.

# Green Synthesis of Fluorescent Carbon Dots for Selective Detection of Tartrazine in Food Samples\_2015

Carbonaceous nanolights, carbon dots (CDs), are attractive alternatives to semiconducting quantum dots owing to their tunable optoelectronic properties, photostability, biocompatibility, water solubility, etc. Although carbon dot composites with metal or metal oxides have been used as visible light photocatalysts for various organic transformations, the role of surface functionality of unsupported CDs on their photocatalytic activity has not been explored. Reported herein, the efficient activity of carboxyl-functionalized CDs as visible light photocatalysts for the C–H oxygenation of alkyl benzene in the presence of tert-butyl hydroperoxide (TBHP) as an external oxidant. Excellent photoinduced electron transfer properties of CDs coupled with photodecomposition of TBHP resulted in C–H bond oxidation with high activity, selectivity, and recyclability under mild reaction conditions. A comparative evaluation suggested the role of surface traps in charge separation and transport efficiency that could account for the high efficiency of the CDs in the oxidation reactions.

# Photoprotection by Plant Extracts: A New Ecological Means To Reduce Pesticide Photodegradation\_2010

Indocyanine green (ICG), an FDA approved medical near-infrared (NIR) imaging agent, has been extensively used in cancer theranosis. However, the limited aqueous photostability, rapid body clearance, and poor cellular uptake severely restrict its practical applications. For these problems to be overcome, ICG-encapsulated hybrid polymeric nanomicelles (PNMs) were developed in this work through coassociation of the amphiphilic diblock copolymer poly(lactic-co-glycolic acid)-b-poly(ethylene glycol) (PLGA-b-PEG) and hydrophobic electrostatic complexes composed of ICG molecules and branched poly(ethylenimine) (PEI). The ICG-encapsulated hybrid PNMs featured a hydrophobic PLGA/ICG/PEI core stabilized by hydrophilic PEG shells. The encapsulation of electrostatic ICG/PEI complexes into the compact PLGA-rich core not only facilitated the ICG loading but also promoted its aqueous optical stability. The effects of the chain length of PEI in combination with ICG on the physiochemical properties of PNMs and their drug leakage were also investigated. PEI10k (10 kDa) could form highly robust and dense complexes with ICG, and thus prominently reduced ICG outflow from the PNMs. The results of in vitro cellular uptake and cytotoxicity studies revealed that the ICG/PEI10k-loaded PNMs significantly promoted cellular uptake of ICG by HeLa cells due to their near-neutral surface, and thereby augmented the NIR-triggered hyperthermia effect in destroying cancer cells. These findings strongly indicate that the ICG/PEI10k-loaded PNMs have significant potential for attaining effective cancer imaging and photothermal therapy.

# Carboxyl-Functionalized Carbon Dots as Competent Visible Light Photocatalysts for Aerobic Oxygenation of Alkyl Benzenes: Role of Surface Functionality\_2018

The newly emerged pathogenic bacteria leads to the bactericides generations one by one, which is definitely a long-term and costly process. For the small organic molecule used as antibacterial materials, photostability, biomembrane penetrating ability, and long-term antibacterial ability still are questionable. In this work, we synthesized the multiple-cation-charged aggregation-induced emission (AIE)-active polymer 1,2-diphenyl-1,2-bis(4-(pyridin-4-yl)phenyl) ethane–1,8-dibromooctane (DBPE-DBO). Due to the incorporating the dark toxicity from positively charged polymers, and the phototoxicity from generation of singlet oxygen, as well as AIE-active fluorescence performance, DBPE-DBO could be employed as an efficient bacteria targeting, imaging, and killing materials. Interestingly, DBPE-DBO was less toxic to the normal mammalian cells, which leads us to verify that DBPE-DBO could be used as a very cell-membrane permeable nucleus imaging probes. Thus, our research results may provide a new concept for the designing advanced biomaterials with versatile antibacterial properties and cell imaging ability.

# Indocyanine Green-Encapsulated Hybrid Polymeric Nanomicelles for Photothermal Cancer Therapy\_2015

A solution blending process for preparation of polymer nanocomposites composed of cationic polyfluorene (PF) and dimethyl sulfoxide (DMSO) -intercalated kaolinite (Ka) clay has been taken to evaluate the effect of Ka nanostructure on the nanocomposite structures, morphology, and properties. Composites containing 2, 5, 7.5, and 10 wt % clay have been characterized with the help of X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), UV–visible spectroscopy, photoluminescence studies, etc. Additionally, the keto defect, inhibition of interchain interaction, and photostability of PF in the nanocomposites have been explored. The XRD and HRTEM studies show the exfoliation of Ka layers at lower content in composites. Intercalation of PF chains into the Ka interlayer space occurs at relatively higher clay content. Nanocomposites exhibit higher thermal stability than pristine PF due to lamination of PF into clay nanogallery through the interchange of DMSO by cationic polyfluorene. The presence of an Si–O–Si stretching band in the composites supports the formation of nanocomposites of PF with Ka. The movement of absorption maxima to higher wavelength indicates the increase of overall conjugation length of PF chains in the nanocomposites. Upon formation of nanocomposite with Ka, the keto defect sites of PF are significantly reduced. This can be attributed to the lamination of single PF chains by Ka interlayer gallery that act as a barrier to oxygen and inhibit the exciton diffusion. Current–voltage characteristics of nanocomposite films have also shown good switching behavior with low forward junction potential.

# Light-Enhanced Bacterial Killing and Less Toxic Cell Imaging: Multicationic Aggregation-Induced Emission Matters\_2018

Carbon quantum dots (C-Dots) have drawn extensive attention in recent years due to their stable physicochemical and photochemical properties. However, the development of nitrogen-doped carbon quantum dots (N-doped C-Dots) is still on its early stage. In this paper, a facile and high-output solid-phase synthesis approach was proposed for the fabrication of N-doped, highly fluorescent carbon quantum dots. The obtained N-doped C-Dots exhibited a strong blue emission with an absolute quantum yield (QY) of up to 31%, owing to fluorescence enhancement effect of introduced N atoms into carbon dots. The strong coordination of oxygen-rich groups on N-doped C-Dots to Fe3+ caused fluorescence quenching via nonradiative electron-transfer, leading to the quantitative detection of Fe3+. The probe exhibited a wide linear response concentration range (0.01–500 μM) to Fe3+ with a detection limit of 2.5 nM. Significantly, the N-doped C-Dots possess negligible cytotoxicity, excellent biocompatibility, and high photostability. All these features are favorable for label-free monitoring of Fe3+ in complex biological samples. It was then successfully applied for the fluorescence imaging of intracellular Fe3+. As an efficient chemosensor, the N-doped C-Dots hold great promise to broaden applications in biological systems.

# Suppression of Keto Defects and Thermal Stabilities of Polyfluorene–Kaolinite Clay Nanocomposites\_2013

Diamond nanoparticles (nanodiamonds) have been recently proposed as new labels for cellular imaging. For small nanodiamonds (size <40 nm), resonant laser scattering and Raman scattering cross sections are too small to allow single nanoparticle observation. Nanodiamonds can, however, be rendered photoluminescent with a perfect photostability at room temperature. Such a remarkable property allows easier single-particle tracking over long time scales. In this work, we use photoluminescent nanodiamonds of size <50 nm for intracellular labeling and investigate the mechanism of their uptake by living cells. By blocking selectively different uptake processes, we show that nanodiamonds enter cells mainly by endocytosis, and converging data indicate that it is clathrin-mediated. We also examine nanodiamond intracellular localization in endocytic vesicles using immunofluorescence and transmission electron microscopy. We find a high degree of colocalization between vesicles and the biggest nanoparticles or aggregates, while the smallest particles appear free in the cytosol. Our results pave the way for the use of photoluminescent nanodiamonds in targeted intracellular labeling or biomolecule delivery.

# Solid-Phase Synthesis of Highly Fluorescent Nitrogen-Doped Carbon Dots for Sensitive and Selective Probing Ferric Ions in Living Cells\_2014

Electronic relaxation pathways in photoexcited nucleobases have received much theoretical and experimental attention due to their underlying importance to the UV photostability of these biomolecules. Multiple mechanisms with different energetic onsets have been proposed by ab initio calculations yet the majority of experiments to date have only probed the photophysics at a few selected excitation energies. We present femtosecond time-resolved photoelectron spectra (TRPES) of the DNA base adenine in a molecular beam at multiple excitation energies between 4.7−6.2 eV. The two-dimensional TRPES data is fit globally to extract lifetimes and decay associated spectra for unambiguous identification of states participating in the relaxation. Furthermore, the corresponding amplitude ratios are indicative of the relative importance of competing pathways. We adopt the following mechanism for the electronic relaxation of isolated adenine; initially the S2(ππ\*) state is populated by all excitation wavelengths and decays quickly within 100 fs. For excitation energies below ∼5.2 eV, the S2(ππ\*)→S1(nπ\*)→S0 pathway dominates the deactivation process. The S1(nπ\*)→S0 lifetime (1032−700 fs) displays a trend toward shorter time constants with increasing excitation energy. On the basis of relative amplitude ratios, an additional relaxation channel is identified at excitation energies above 5.2 eV.

# Photoluminescent Diamond Nanoparticles for Cell Labeling: Study of the Uptake Mechanism in Mammalian Cells\_2009

Nanostructured Ag nanoparticles (Ag-NPs)/nanoporous ZnO micrometer-rods (n-ZnO MRs) have been synthesized by a two-step method. The n-ZnO MRs was initially prepared by solvothermal-assisted heat treatment. The rods had the diameter ranged from 90 to 150 nm and length between 0.5 and 3 μm. They were found to be porous and were composited of ZnO nanopartiles with size of about 20 nm. In the second stage, Ag-NPs with a diameter of 20–50 nm were anchored onto the surface of the as-prepared n-ZnO MRs by a photoreduction method. The Ag-NPs/n-ZnO MRs were evaluated for their ability to degrade methylene blue (MB) solution under visible to ultraviolet (UV) light irradiation. The rate of degradation of the as-prepared Ag-NPs/n-ZnO MRs was more than twice and nearly 5.6 times faster than that of using bare n-ZnO MRs under the UV and solar light irradiation, respectively. The formation of Schottky barriers in the regions between the Ag-NPs and n-ZnO MRs had improved the charge separation and consequently enhanced the efficiency of the degradation process. Moreover, the as-prepared hybrid structure exhibited high photostability, and 98% of degradation efficiency could be maintained even after being used five times. This endurance was attributed to the retardation of photocorrosion of ZnO as a result of the low concentration of surface defects in the as-prepared n-ZnO MRs. It also minimized the surface defects of the as-prepared n-ZnO MRs and consequently further inhibited the photocorrosion of ZnO when the deposited Ag-NPs were much more inclined to combine with the chemisorbed oxygen.

# Wavelength Dependence of Electronic Relaxation in Isolated Adenine Using UV Femtosecond Time-Resolved Photoelectron Spectroscopy\_2010

The direct covalent attachment of conducting polymers (CP) to nanoparticles (NP) to form CP-NP nanohybrids is of great interest for optoelectronic device applications. Hybrids formed by covalently anchoring CP to NP, rather than traditional blending or bilayer approaches, is highly desirable. CP-NP nanohybrids have increased interfacial surface area between the two components, facilitating rapid exciton diffusion at the p–n heterojunction. These materials take advantage of the facile solution processability, lightweight characteristics, flexibility, and mechanical strength associated with CPs, and the broad spectral absorption, photostability, and high charge carrier mobility of NPs. We demonstrate the ability to polymerize a hole transporting (HT) polymer utilizing reversible-addition–fragmentation chain transfer (RAFT) polymerization and its subsequent rapid aminolysis to yield a thiol-terminated HT polymer. Subsequent facile attachment to gold (Au) and silver (Ag) NPs and cadmium selenide (CdSe) quantum dots (QDs), to form a number of CP–NP systems is demonstrated and characterized. CP–NP nanohybrids show broad spectral absorptions ranging from UV through visible to the near IR, and their facile synthesis and purification could allow for large scale industrial applications.

# Ag Nanoparticle Decorated Nanoporous ZnO Microrods and Their Enhanced Photocatalytic Activities\_2012

In this article, luminescent properties of gold nanoclusters (AuNCs) were studied at the single nanoparticle level and also used as novel imaging agents in cell media. Two types of water-soluble AuNCs which were stabilized with a monolayer composed of either mercaptosuccinic acid (MSA) or tiopronin thiolate ligands were synthesized by a chemical reduction reaction. These AuNCs were determined to have an average core diameter of less than 2 nm. On a time-resolved confocal microscope, the emission signals from the single AuNCs were distinctly recordable. The quantum yields of these AuNCs were measured to be ca. 5%. The lifetime of these AuNCs is also much longer than the lifetime of cellular autofluorescence in lifetime cell imaging as well as the lifetime of organic dye Alexa Fluor 488. After being derivatized with polyethylene glycol (PEG) moieties, the AuNCs were uploaded efficiently in the HeLa cells. Fluorescence intensity and lifetime cell images were recorded on the time-resolved confocal microscope in which the emission from the AuNCs was readily differentiated from the cellular autofluorescence background because of their relatively stronger emission intensities and longer lifetimes. These loaded nanoclusters in the cells were observed to widely distribute throughout the cells and especially densely loaded near the cell nucleuses. The AuNCs in the cells were also tested to have a better photostability relative to the organic fluorophores under the same conditions. We thus conclude that the AuNCs have a great potential as novel nanoparticle imaging agents, especially as lifetime imaging agents, in fluorescence imaging applications. We also prospect much broader applications of these AuNCs after further improvements of their luminescence quantum yields.

# Synthesis of Conducting Polymer–Metal Nanoparticle Hybrids Exploiting RAFT Polymerization\_2015

The dicyanomethylenedihydrofuran (DCDHF) class of single-molecule fluorophores contains an amine donor and a dicyanomethylenedihydrofuran acceptor linked by a conjugated unit (benzene, naphthalene, or styrene). Molecules in this class have a number of useful properties in addition to those usually required for single-molecule studies (such as high fluorescence quantum yield and photostability), including second-order optical nonlinearity, large ground-state dipole moment, and sensitivity to local environment. Moreover, most DCDHF molecules have amphiphilic structures, with a polar dicyanomethylenedihydrofuran headgroup and nonpolar hydrocarbon tails on the amine or furan ring, and can be used as fluorescent lipid analogues for live cell imaging. Here we demonstrate that individual molecules of several different DCDHF lipid analogues can be observed diffusing in the plasma membrane of Chinese hamster ovary cells. The photophysical and diffusive behaviors of the DCDHF lipid analogues in membranes are described and are found to be competitive with the well-known lipid probe N-(6-tetramethylrhodaminethiocarbamoyl)-1,2-dihexadecanoyl-sn-glycero-3-phosphoethanolamine.

# Fluorescence Intensity and Lifetime Cell Imaging with Luminescent Gold Nanoclusters\_2012

The dicyanomethylenedihydrofuran (DCDHF) class of single-molecule fluorophores contains an amine donor and a dicyanomethylenedihydrofuran acceptor linked by a conjugated unit (benzene, naphthalene, or styrene). Molecules in this class have a number of useful properties in addition to those usually required for single-molecule studies (such as high fluorescence quantum yield and photostability), including second-order optical nonlinearity, large ground-state dipole moment, and sensitivity to local environment. Moreover, most DCDHF molecules have amphiphilic structures, with a polar dicyanomethylenedihydrofuran headgroup and nonpolar hydrocarbon tails on the amine or furan ring, and can be used as fluorescent lipid analogues for live cell imaging. Here we demonstrate that individual molecules of several different DCDHF lipid analogues can be observed diffusing in the plasma membrane of Chinese hamster ovary cells. The photophysical and diffusive behaviors of the DCDHF lipid analogues in membranes are described and are found to be competitive with the well-known lipid probe N-(6-tetramethylrhodaminethiocarbamoyl)-1,2-dihexadecanoyl-sn-glycero-3-phosphoethanolamine.

# Diffusion of Lipid-like Single-Molecule Fluorophores in the Cell Membrane\_2006

Bulk HgS itself has proven to be a technologically important material; however, the poor stability and weak emission of HgS nanocrystals have greatly hindered their promising applications. Presently, a critical problem is the uncontrollable growth of HgS NCs and their intrinsic surface states which are susceptible to the local environment. Here, we address the issue by an ion-tuning approach to fabricating stable, highly fluorescent Cd:HgS/CdS NCs for the first time, which efficiently tuned the band-gap level of HgS NCs, pushing their intrinsic states far away from the surface, reducing the strong interaction of the environment with surface states and hence drastically boosting the exciton transition. As compared to bare HgS NCs, the obtained Cd:HgS/CdS NCs exhibited tunable luminescence peaks from 724 to 825 nm with an unprecedentedly high quantum yield up to 40% at room temperature and excellent thermal and photostability. Characterized by TEM, XRD, XPS, and AAS, the resultant Cd:HgS/CdS NCs possessed a zinc-blende structure and was composed of a homogeneous alloyed HgCdS structure coated with a thin-layer CdS shell. The formation mechanism of Cd:HgS/CdS NCs was proposed. These bright, stable HgS-based NCs presented promising applications as fluorescent inks for anticounterfeiting and as excellent light converters when coated onto a blue-light-emitting diode.

# Understanding the Electronic Structure of Isoindigo in Conjugated Systems: A Combined Theoretical and Experimental Approach.\_2013

Nitrogen-vacancy (NV–) defects embedded in nanodiamond have attracted attention for their useful photonic and spin properties and their exceptional photostability. Efficiently detecting nanodiamonds that possess color centers and discriminating from any background fluorescent contamination are essential for nanodiamond-based technologies and thus necessitates the detection of both the nanoparticle and the fluorescent signature. However, optically detecting small nanodiamonds (<40 nm) proves difficult due to the low absorption and scattering cross section of nanodiamonds. Here we demonstrate an all-optical method capable of simultaneously colocalizing scattered signal from individual nanodiamonds (∼10 nm) with the fluorescent signature from NV– centers.

# Highly Fluorescent, Near-Infrared-Emitting Cd2+-Tuned HgS Nanocrystals with Optical Applications\_2015

With the increasing demand for confocal and two-photon fluorescence imaging, the availability of reactive probes that possess high two-photon absorptivity, high fluorescence quantum yield, and high photostability is of paramount importance. To address the demand for better-performing probes, we prepared two-photon absorbing amine-reactive fluorenyl-based probes 2-(9,9-bis(2-(2-methoxyethoxy)ethyl)-2-isothiocyanato-9H-fluoren-7-yl)benzothiazole (1) and 2-(4-(2-(9,9-bis(2-(2-ethoxyethoxy)ethyl)-2-isothiocyanato-9H-fluoren-7-yl)vinyl)phenyl)benzothiazole (2), incorporating the isothiocyanate as a reactive linker. Probe design was augmented by integrating high optical nonlinearities, increased hydrophilicity, and coupling with reactive functional groups for specific targeting of biomolecules, assuring a better impact on two-photon fluorescence microscopy (2PFM) imaging. The isothiocyanate (NCS) derivatives were conjugated with cyclic peptide RGDfK and Reelin protein. The study of the chemical and photophysical properties of the new labeling reagents, as well as the conjugates, is described. The conjugates displayed high chemical stability and photostability. The NCS derivatives had low fluorescence quantum yields, while their bioconjugates exhibited high fluorescence quantum yields, essentially “lighting up” after conjugation. Conventional and 2PFM imaging and fluorescence lifetime imaging (FLIM) of HeLa, NT2, and H1299 cells, incubated with two-photon absorbing amine-reactive probe (1), RGDfK-dye conjugate (7), and Reelin-dye conjugate (6), was demonstrated.

# All-Optical Method for Characterizing Individual Fluorescent Nanodiamonds\_2016

Enzyme-assisted detection strategies of microRNAs (miRNAs) in vitro have accomplished both great sensitivity and specificity. However, low expression of miRNAs and a complex environment in cells induces big challenges for monitoring and tracking miRNAs in vivo. The work reports the attempt to carry miRNA imaging into live cells, by enzyme-aided recycling amplification. We utilize facile probes based yellow aggregation-induced emission luminogens (AIEgens) with super photostable property but without quencher, which are applied to monitor miRNAs not only from urine sample extracts (in vitro) but also in live cells (in vivo). The assay could distinguish the cancer patients’ urine samples from the healthy urine due to the good specificity. Moreover, the probe showed much higher fluorescence intensity in breast cancer cells (MCF-7) (miR-21 in high expression) than that in cervical cancer cells (HeLa) and human lung fibroblast cells (HLF) (miR-21 in low expression) in more than 60 min, which showed the good performance and super photostability for the probe in vivo. As controls, another two probes with FAM/Cy3 and corresponding quenchers, respectively, could perform miRNAs detections in vitro and parts of in vivo tests but were not suitable for the long-term cell tracking due to the photobleach phenomena, which also demonstrates that the probe with AIEgens is a potential candidate for the accurate identification of cancer biomarkers.

# Amine-Reactive Fluorene Probes: Synthesis, Optical Characterization, Bioconjugation, and Two-Photon Fluorescence Imaging\_2008

An efficient and stable CuO-TiO2 nanocomposite photocatalyst was synthesized by using the simple molten-salt method. Characterization by HR-TEM confirmed the existence of both TiO2 and CuO in the nanocomposite, revealing hexagonal TiO2 nanoparticles (NPs) with average particles size of 23.8 nm. CuO QDs decorated on the TiO2 surface were in the range of 2.2 to 4.6 nm. Photocatalytic experiments for hydrogen (H2) production were carried out under an LED (λ = 365 nm) lamp and natural solar light. The effect of Cu-loading in CuO-TiO2 NCs and synthesis time were studied. The optimized CuO-TiO2 NCs abbreviated as CuT-4 and CuT-3 showed 27.7- and 9.0-fold superior rate of H2 production compared to pristine TiO2 NPs under LED and solar irradiation, respectively. At optimal conditions, CuO-TiO2 NCs demonstrated good photostability for H2 evolution during 75 h illumination under LED light. The experimental results confirmed the cocatalytic role of CuO for improved H2 generation by a minimized recombination of excitons.

# Live Cell MicroRNA Imaging Using Exonuclease III-Aided Recycling Amplification Based on Aggregation-Induced Emission Luminogens\_2016

A new class of nanocrystal quantum dot (NQD), the “giant” NQD (g-NQD), was investigated for its potential to address outstanding issues associated with the use of NQDs as down-conversion phosphors in light-emitting devices, namely, insufficient chemical/photostability and extensive self-reabsorption when packed in high densities or in thick films. Here, we demonstrate that g-NQDs afford significantly enhanced operational stability compared to their conventional NQD counterparts and minimal self-reabsorption losses. The latter results from a characteristic large Stokes shift (>100 nm; >0.39 eV), which itself is a manifestation of the internal structure of these uniquely thick-shelled NQDs. In carefully prepared g-NQDs, light absorption occurs predominantly in the shell but emission occurs exclusively from the core. We directly compare for the first time the processes of shell→core energy relaxation and core→core energy transfer by evaluating CdS→CdSe down-conversion of blue→red light in g-NQDs and in a comparable mixed-NQD (CdSe and CdS) thin film, revealing that the internal energy relaxation process affords a more efficient and color-pure conversion of blue to red light compared to energy transfer. Lastly, we demonstrate the facile fabrication of white-light devices with correlated color temperature tuned from ∼3200 to 5800 K.

# CuO Quantum Dots Decorated TiO2 Nanocomposite Photocatalyst for Stable Hydrogen Generation\_2017

Fluorescent nanoparticles (NPs) have become irreplaceable tools for advanced cellular and subcellular imaging. While very bright NPs require excitation with UV or visible light, which can create strong autofluorescence of biological components, NIR-excitable NPs without autofluorescence issues exhibit much lower brightness. Here, we show the application of a new type of surface-photosensitized terbium NPs (Tb-NPs) for autofluorescence-free intracellular imaging in live HeLa cells. The combination of exceptionally high brightness, high photostability, and long photoluminecence (PL) lifetimes for highly efficient suppression of the short-lived autofluorescence allowed for time-gated PL imaging of intracellular vesicles over 72 h without toxicity and at extremely low Tb-NP concentrations down to 12 pM. Detection of highly resolved long-lifetime (ms) PL decay curves from small (∼10 μm2) areas within single cells within a few seconds emphasized the unprecedented photophysical properties of Tb-NPs for live-cell imaging that extend well beyond currently available nanometric imaging agents.

# Giant Nanocrystal Quantum Dots: Stable Down-Conversion Phosphors that Exploit a Large Stokes Shift and Efficient Shell-to-Core Energy Relaxation\_2012

In this work, we develop a ratiometric two-photon fluorescent probe, ATD@QD-E2Zn2SOD (ATD = amino triphenylamine dendron, QD = CdSe/ZnSe quantum dot, E2Zn2SOD = Cu-free derivative of bovine liver copper–zinc superoxide dismutase), for imaging and sensing the changes of intracellular Cu2+ level with clear red-to-yellow color change based on specific biomolecular recognition of E2Zn2SOD for Cu2+ ion. The inorganic–organic nanohybrided fluorescent probe features two independent emission peaks located at 515 nm for ATD and 650 nm for QDs, respectively, under two-photon excitation at 800 nm. Upon addition of Cu2+ ions, the red fluorescence of QDs drastically quenches, while the green emission from ATD stays constant and serves as a reference signal, thus resulting in the ratiometric detection of Cu2+ with high accuracy by two-photon microscopy (TPM). The present probe shows high sensivity, broad linear range (10–7–10–3 M), low detection limit down to ∼10 nM, and excellent selectivity over other metal ions, amino acids, and other biological species. Meanwhile, a QD-based inorganic-organic probe demonstrates long-term photostability, good cell-permeability, and low cytotoxicity. As a result, the present probe can visualize Cu2+ changes in live cells by TPM. To the best of our knowledge, this is the first report for the development of a QD-based two-photon ratiometric fluorescence probe suitable for detection of Cu2+ in live cells.

# Autofluorescence-Free Live-Cell Imaging Using Terbium Nanoparticles\_2018

Photolysis (λ = 254 nm) of 4-allyl-tetrazolones 2a−c was carried out in methanol, 1-propanol, 1-hexanol, acetonitrile, and cyclohexane. The sole primary photochemical process identified was molecular nitrogen elimination, with formation of pyrimidinones 6a−c. Following the primary photocleavage, secondary reactions were observed in acetonitrile and cyclohexane, leading to phenyl-isocyanate (7), aniline (9), and 1-phenylprop-1-enyl-isocyanate (10a). In alcoholic solutions, the primary products, 6a−c, remained photostable even under extended irradiation, making possible the isolation of 3,4-dihydro-pyrimidinones as stable compounds in very high yields. The observed photostability of pyrimidinones 6a−c in alcohols is ascribed to the excited state quenching via reversible proton transfer, facilitated by the solvent cage stabilization due to formation of hydrogen bonds. The viscosity of alcohols is directly related to the cage effects observed. The photocleavage of 4-allyl-tetrazolones leads probably to a caged triplet radical pair. This hypothesis is confirmed by the solvent viscosity effect on the photolysis quantum yields. Additionally, dissolved molecular oxygen sensitizes the formation of pyrimidinones, as should be expected for a triplet intermediate that can only form the product molecule after T−S conversion, which is accelerated by oxygen.

# Two-Photon Ratiometric Fluorescent Sensor Based on Specific Biomolecular Recognition for Selective and Sensitive Detection of Copper Ions in Live Cells\_2013

Colloidal core/shell InP/ZnSe quantum dots (QDs), recently produced using an improved synthesis method, have a great potential in life-science applications as well as in integrated quantum photonics and quantum information processing as single-photon emitters. Single-particle spectroscopy of 10 nm QDs with 3.2 nm cores reveals strong photon antibunching attributed to fast (70 ps) Auger recombination of multiple excitons. The QDs exhibit very good photostability under strong optical excitation. We demonstrate that the antibunching is preserved when the QDs are excited above the saturation intensity of the fundamental-exciton transition. This result paves the way toward their usage as high-purity on-demand single-photon emitters at room temperature. Unconventionally, despite the strong Auger blockade mechanism, InP/ZnSe QDs also display very little luminescence intermittency (“blinking”), with a simple on/off blinking pattern. The analysis of single-particle luminescence statistics places these InP/ZnSe QDs in the class of nearly blinking-free QDs, with emission stability comparable to state-of-the-art thick-shell and alloyed-interface CdSe/CdS, but with improved single-photon purity.

# Mechanistic Investigations into the Photochemistry of 4-Allyl-tetrazolones in Solution:  A New Approach to the Synthesis of 3,4-Dihydro-pyrimidinones\_2006

In this study, biocompatible and proton-resistant CdSe quantum dots (QDs) assembled on gelatin nanospheres (GNs) have been synthesized by combining the two-step desolvation method with the layer-by-layer assembly technique. The core–shell fluorescent gelatin nanosphere consists of a gelatin core and a four-layer shell of hydrophilic CdSe QDs assembled through polyelectrolytes (PE). The morphology, microstructures, and photostability of the hybrid spheres were further investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), fluorospectrometery, and confocal fluorescent microscopy (CFM), respectively. The average diameter of the hybrid QDs-gelatin nanospheres (QDs-GNs) is estimated at 484 ± 40 nm. Our results indicate that the 20 ± 5 nm of the shell is attributed to the four–layer of CdSe QDs assembled through the PE. QD-GNs show a strong photoluminescence with the maximum emission (λem) at 613 nm at the excitation wavelength of 470 nm. The core–shell QDs-GNs are able to resist quenching in acidic solution (pH < 4). Furthermore, core–shell QDs-GNs show a longer lifetime in a broad range of pH values, from 9 to 1. The calculated average lifetime (τave) of QDs-GNs is about 889 ± 23 ps, which is 3-fold longer than that of MUA-QDs (263 ± 10 ps) at pH 7.0. The enhanced lifetime of QDs-GNs is almost 9 times of that of CdSe QDs when pH value is 1. Meanwhile, the cell viability study shows that no significant toxic effect is imposed on the NIH/3T3 mouse fibroblast cell line when the concentration of QD-GNs is below 5 mg/mL. It is expected that this new biocompatible fluorescent nanospheres could be an excellent alternative fluorescent imaging agent for cell labeling, especially in acidic conditions.

# Nearly Blinking-Free, High-Purity Single-Photon Emission by Colloidal InP/ZnSe Quantum Dots\_2017

Nanoscale carbon materials hold great promise for biotechnological and biomedical applications. Fluorescent nanodiamond (FND) is a recent new addition to members of the nanocarbon family. Here, we report long-term in vivo imaging of FNDs in Caenorhabditis elegans (C. elegans) and explore the nano-biointeractions between this novel nanomaterial and the model organism. FNDs are introduced into wild-type C. elegans by either feeding them with colloidal FND solution or microinjecting FND suspension into the gonads of the worms. On feeding, bare FNDs stay in the intestinal lumen, while FNDs conjugated with biomolecules (such as dextran and bovine serum albumin) are absorbed into the intestinal cells. On microinjection, FNDs are dispersed in the gonad and delivered to the embryos and eventually into the hatched larvae in the next generation. The toxicity assessments, performed by employing longevity and reproductive potential as physiological indicators and measuring stress responses with use of reporter genes, show that FNDs are stable and nontoxic and do not cause any detectable stress to the worms. The high brightness, excellent photostability, and nontoxic nature of the nanomaterial have enabled continuous imaging of the whole digestive system and tracking of the cellular and developmental processes of the living organism for several days.

# Development of Biocompatible and Proton-Resistant Quantum Dots Assembled on Gelatin Nanospheres\_2014

Comprehensive investigations of the linear and nonlinear optical properties of new Ir(III) complexes [Ir(pbt)2(dbm)] (1), [Ir(pbt)2(dmac)] (2), and [Ir(pbt)2(minc)] (3) (pbt = 2-phenylbenzothiazole; dbm = dibenzoyl methane; dmac = (1E,4Z,6E)-1,7-bis(4-(dimethylamino)phenyl)-5-hydroxyhepta-1,4,6-trien-3-one; minc = (1E,4Z,6E)-5-hydroxy-1,7-bis(1-methyl-1H-indol-3-yl)hepta-1,4,6-trien-3-one) are reported, including photostability, two-photon absorption, and femtosecond transient absorption spectroscopy. The steady-state and time-resolved spectral properties of 1–3 revealed the electronic nature of the absorption bands, and photoluminescence emission of 2 and 3 shows both fluorescence and phosphorescence processes occurring simultaneously in liquid solution at room temperature. This unusual behavior of 2 and 3 can be explained by a dual-minimum potential surface of the excited electronic state resulting in two independent fluorescence and phosphorescence emission channels. The degenerate 2PA spectra of 1–3 were obtained by open aperture Z-scans with a femtosecond laser, and maxima values of 2PA cross sections up to ∼350 GM were observed. Ultrafast relaxation processes of 1–3 were investigated by femtosecond transient absorption, and the characteristic times for triplet formation were determined to be <500 fs for 1 and ∼2 ps for 2 and 3 in a nonpolar medium.

# In Vivo Imaging and Toxicity Assessments of Fluorescent Nanodiamonds in Caenorhabditis elegans\_2010

Excitation energy transfer involving semiconductor quantum dots (QDs) has received increased attention in recent years because their properties, such as high photostability and size-tunable optical properties, have made QDs attractive as Förster resonant energy transfer (FRET) probes or sensors. An intriguing question in FRET studies involving QDs has been whether the dipole approximation, commonly used to predict the electronic coupling, is sufficiently accurate. Accurate estimates of electronic couplings between two 3.9 nm CdSe QDs and between a QD and a chlorophyll molecule are reported. These calculations are based on transition densities obtained from atomistic semiempirical calculations and time-dependent density functional theory for the QD and the chlorophyll, respectively. In contrast to the case of donor−acceptor molecules, where the dipole approximation breaks down at length scales comparable to the molecular dimensions, we find that the dipole approximation works surprisingly well when donor and/or acceptor is a spherical QD, even at contact donor−acceptor separations. Our conclusions provide support for the use of QDs as FRET probes for accurate distance measurements.

# Electronic Nature of New Ir(III) Complexes: Linear Spectroscopic and Nonlinear Optical Properties\_2017

Conspectus  
Visible-light photoredox catalysis offers exciting opportunities to achieve challenging carbon–carbon bond formations under mild and ecologically benign conditions. Desired features of photoredox catalysts are photostability, long excited-state lifetimes, strong absorption in the visible region, and high reduction or oxidation potentials to achieve electron transfer to substrates, thus generating radicals that can undergo synthetic organic transformations. These requirements are met in a convincing way by RuII(phenanthroline)3- and IrIII(phenylpyridine)3-type complexes and, as a low-cost alternative, by organic dyes that offer a metal-free catalyst but suffer in general from lower photostability. CuI(phenanthroline)2 complexes have been recognized for more than 30 years as photoresponsive compounds with highly negative Cu(I)\* → Cu(II) oxidation potentials, but nevertheless, they have not been widely considered as suitable photoredox catalysts, mainly because their excited lifetimes are shorter by a factor of 5 to 10 compared with Ru(II) and Ir(III) complexes, their absorption in the visible region is weak, and their low Cu(II) → Cu(I) reduction potentials might impede the closure of a catalytic cycle for a given process. Contrasting again with RuIIL3 and IrIIIL3 complexes, CuIL2 assemblies undergo more rapid ligand exchange in solution, thus potentially reducing the concentration of the photoactive species. Focusing on atom transfer radical addition (ATRA) reactions and related processes, we highlight recent developments that show the utility of CuI(phenanthroline)2 complexes as photoredox catalysts, demonstrating that despite their short excited-state lifetimes and weak absorption such complexes are efficient at low catalyst loadings. Moreover, some of the inherent disadvantages stated above can even be turned to advantages: (1) the low Cu(II) → Cu(I) reduction potential might efficiently promote reactions via a radical chain pathway, and (2) the tendency for ligand exchange in CuIL2 assemblies allows the efficient synthesis of heteroleptic CuILL′ complexes to tune the steric and electronic properties and also might coordinate and thus activate substrates in the course of a reaction in addition to electron transfer. Moreover, new photoredox cycles have also been discovered beyond the visible-light-induced Cu(I)\* → Cu(II) electron transfer that is arguably best known: examples of the Cu(II)\* → Cu(I) and Cu(I)\* → Cu(0) transitions have been realized, greatly broadening the potential for copper-based photoredox-catalyzed transformations. Finally, a number of organic transformations that are unique to Cu(I) photoredox catalysts have been discovered.

# Examining Förster Energy Transfer for Semiconductor Nanocrystalline Quantum Dot Donors and Acceptors\_2008

A facile approach of layer-by-layer depositing and hydrolysis of FeCl3 is developed to fabricate 3D-ordered Fe2O3 film. The 3D-ordered Fe2O3 film was characterized by SEM, XRD, and DRUV−vis. It has 3D-ordered interconnecting macropores (340 nm) with nanocrystalline hematite Fe2O3 walls (27.2 nm). The 3D-ordered macroporous nanocrystalline Fe2O3 film exhibits 2.4 times larger photocatalytic activity for the photodegradation of dye in the presence of H2O2 under visible irradiation than the nanocrystalline α-Fe2O3 film without macropores and very good photostability. The much higher photocatalytic activity of the 3D-ordered macroporous nanocrystalline Fe2O3 film than that of the reference Fe2O3 film is attributed to the unique nanostructure and architecture of the 3D-ordered Fe2O3 film, which result in the much greater light harvesting efficiency and efficient mass transport in the former than in the latter due to the existence of 3D-ordered interconnecting macropores. The effect of photonic stop band on the photocatalytic activity of the 3D-ordered Fe2O3 film was studied by angle-dependent solid-state photodegradation experiments with monochromatic irradiation. A slow photon enhancement of photocatalytic activity was achieved by adjusting the red edge of the photonic stop band of the 3D-ordered Fe2O3 film close to the electronic bandgap of Fe2O3. The photodegradation mechanism of crystal violet on the 3D-ordered Fe2O3 photocatalyst in the presence or absence of H2O2 was discussed.

# Shining Light on Copper: Unique Opportunities for Visible-Light-Catalyzed Atom Transfer Radical Addition Reactions and Related Processes\_2016

There is growing interest in the bis-tridentate Ir(III) emitters as they are expected to display both improved emission efficiency and improved photostability. Herein, we turned to the new emitters m2h-1–3 and m6h-1–3, bearing a pincer carbene ancillary and a chromophoric chelate derived from judiciously selected phenyl-pyrimidine-pyrazole entities (pzm2hF)H2 and (pzm6hF)H2, which differ in terms of the location of phenyl and pyrazole substituents on the central pyrimidine. Density functional theory calculations revealed a notable change in the spin density distribution from the pyrimidine-pyrazolate entity in m2h to the pyrimidine-phenyl fragment in m6h. As a consequence, the m6h emitters exhibited both shortened emission lifetimes and improved stabilities during extensive photolysis in solution, while corresponding organic light-emitting diodes (OLEDs) doped with green-emitting m6h-1 and sky-blue-emitting m6h-2 and m6h-3 exhibited external quantum efficiencies of 17.6, 15.9, and 17.6%, respectively, superior to those of all of their m2h counterparts at a practical luminance of 103 cd/m2. This finding suggests a new methodology for fine-tuning the electronic transition that is important to high-performance and durable phosphorescent OLEDs.

# Facile Fabrication of 3D-Ordered Macroporous Nanocrystalline Iron Oxide Films with Highly Efficient Visible Light Induced Photocatalytic Activity\_2010

The rapid development in fluorescence microscopy and imaging techniques has greatly benefited our understanding of the mechanisms governing cellular processes at the molecular level. In particular, super-resolution microscopy methods overcome the diffraction limit to observe nanoscale cellular structures with unprecedented detail, and single-molecule tracking provides precise dynamic information about the motions of labeled proteins and oligonucleotides. Enhanced photostability of fluorescent labels (i.e., maximum emitted photons before photobleaching) is a critical requirement for achieving the ultimate spatio-temporal resolution with either method. While super-resolution imaging has greatly benefited from highly photostable fluorophores, a shortage of photostable fluorescent labels for bacteria has limited its use in these small but relevant organisms. In this study, we report the use of a highly photostable fluoromodule, dL5, to genetically label proteins in the Gram-negative bacterium Caulobacter crescentus, enabling long-time-scale protein tracking and super-resolution microscopy. dL5 imaging relies on the activation of the fluorogen Malachite Green (MG) and can be used to label proteins sparsely, enabling single-protein detection in live bacteria without initial bleaching steps. dL5-MG complexes emit 2-fold more photons before photobleaching compared to organic dyes such as Cy5 and Alexa 647 in vitro, and 5-fold more photons compared to eYFP in vivo. We imaged fusions of dL5 to three different proteins in live Caulobacter cells using stimulated emission depletion microscopy, yielding a 4-fold resolution enhancement compared to diffraction-limited imaging. Importantly, dL5 fusions to an intermediate filament protein CreS are significantly less perturbative compared to traditional fluorescent protein fusions. To the best of our knowledge, this is the first demonstration of the use of fluorogen activating proteins for super-resolution imaging in live bacterial cells.