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Colloidal Quantum Dots: Think Outside the (Particle-in-a-)Box

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ABSTRACT: This Perspective discusses recent work on mechanisms by which organic ligands affect the electronic structure and exciton dynamics of colloidal quantum dots (QDs). Much of the work described here uses some combination of steady-state absorption, transient absorption, steady-state photoluminescence, and transient photoluminescence spectroscopies to characterize QD–ligand complexes. Ligands affect the ground-state electronic structure of QDs via mixing of the frontier orbitals at the QD–ligand interface and influence the dynamics of excitonic decay by mediating charge trapping or by participating in charge transfer. This Perspective highlights strategies to address the various forms of structural and chemical heterogeneity of QD ensembles in identifying the mechanisms of these ligand-mediated processes. Finally, four-wave mixing techniques are discussed as promising methods for direct measurement of ligand-mediated nonradiative dissipation of the QD exciton.
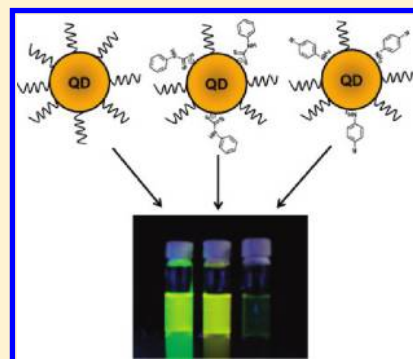
One feature common to all nanostructures is a high ratio of surface area to volume relative to bulk materials. Within a spherical colloid with a diameter of 5 nm, approximately 40% of the atoms are on the surface. These surfaces are, in the case of colloidal semiconductor nanocrystals or quantum dots (QDs), chemically disordered terminations of single-crystal lattices, where ions experience a range of degrees of coordination. Along with polydispersity in size, surface chemistry is the major source of heterogeneity in the optical properties of QDs, both in time, which manifests as PL intermittency or "blinking", and within an ensemble of particles. The heterogeneous and dynamic nature of QD surfaces complicates efforts to understand the mechanisms by which surface chemistry influences the optical properties of QDs; however, achieving an understanding of these mechanisms will enable us to optimize the properties of QDs for applications such as photovoltaics, photocatalysis, and LEDs through rational design of surface chemistry.

Recent work has shown that surface-mediated processes dictate the probability of several of the most interesting and potentially useful photophysical phenomena observed for colloidal QDs. For example, the "phonon bottleneck" arises from the mismatch between the energy spacings of the quantized electronic energy levels within the conduction and valence bands of the QD and the energies of core lattice phonons.[1] This energy mismatch, in principle, slows the cooling of hot carriers (electrons or holes excited to energies higher than the conduction or valence band edge states) to the band edge relative to their cooling rates in bulk semiconductors. Hot electrons, however, can break the phonon bottleneck and cool to the edge of the conduction band via a fast Auger process that transfers the excess energy to the hole.[2] Guyot-Sionnest et al.[3] and Klimov et al.[4] demonstrated that certain organic ligands, when present on the surface of the QD, can efficiently trap holes and prevent them from participating in

the Auger process, thereby preserving the bottleneck effect. In CdSe QDs, energy levels within the valence band are more closely spaced than levels within the conduction band; therefore, there is no Auger channel by which hot holes can break the phonon bottleneck. Cooney et al.[5] showed, however, that hot hole relaxation rates in CdSe QDs are not consistent with the presence of a phonon bottleneck and suggested that hot holes relax via nonadiabatic coupling with ligand vibrations.

Hot carriers with sufficient energy can form a second exciton upon relaxing to the band edge through an inverse Auger process known as carrier multiplication or multiple exciton generation (MEG). Quantum confinement enhances the probability of this process. Carrier multiplication yields of as high as 700% have been reported for PbSe QDs.[6] These yields are typically measured typically by dividing the amplitude of the ground-state bleach feature in a transient absorption spectrum immediately after photoexcitation has created the multi-excitonic state by the amplitude of the bleach feature hundreds of picoseconds after photoexcitation when only one exciton remains in the QD. Recent work has suggested that the presence of surface states results in slow-rising positive transient absorption features that overlap with the ground-state bleach feature and reduce its amplitude at long delay times, which leads to inflated measurements of carrier multiplication yields.[7] The ability to extract either multiple carriers or hot carriers from QDs upon the absorption of a single photon drastically increases the theoretical efficiency of QD-based photovoltaics. There is accumulating evidence that an understanding of the contribution of the surface chemistry of QDs to their electronic structure and dynamics is the key to exploiting the desirable properties that should accompany quantum confinement.

There are many well-developed strategies for chemically stabilizing and passivating the nanocrystalline cores of colloidal QDs. Inorganic shells are useful for preserving photoluminescence of the cores[8] and for eliminating low-dielectric (i.e., electrically resistive) organic material from solid-state films of QDs.[9] Organic and organometallic molecules as surface ligands, however, offer more flexibility in design parameters than semiconductor shells and permit variation in the nature of the core−ligand interaction (coordinate covalent, dative, electrostatic, van der Waals), the denticity of the core−ligand bond, the composition of the ligand layer (pure or mixed monolayer), the dielectric constant of the ligand layer, and the energies of filled and unfilled frontier orbitals, defined as the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, in the ligand layer. Here, we explore three functions that organic ligands can perform with respect to the electronic structure and exciton dynamics of colloidal quantum dots, (i) changing the degree of quantum confinement of the exciton through mixing with QD orbitals in the ground state, (ii) passivating incompletely coordinated metal ions on the QD surface, and (iii) exchanging electrons with the photoexcited QD.

> The potential of the organic approach for controlling QD photophysics lies in the power of synthetic chemistry to produce a large range of electronic structures and adsorption chemistries with small synthetic adjustments.

The examples of QD−ligand interactions (and the properties of QD−ligand complexes that result from them) that we outline here are intended to illustrate that organic molecules can perform all of the functions that inorganic shells can perform with respect to controlling the optical properties of QDs. This control is achievable through the design of every functional group in the molecule, not only the adsorbing head group. Given this design space, the library of possible organic and organometallic ligands for QDs is much larger than the library of inorganic shell compounds, and we believe that the potential of the organic approach for controlling QD photophysics lies in the power of synthetic chemistry to produce a large range of electronic structures and adsorption chemistries with small synthetic adjustments. The categories of QD−ligand interactions that we present below are one way to organize strategies for realizing this potential and a starting point for producing QD−ligand complexes with properties beyond those of their isolated components.

Dictating the Electronic Structure of the Exciton through Ground-State QD−Ligand Interactions. The shape and energy of the wave functions of excitonic charge carriers are sensitive to the finite potential barrier presented by the ligands that passivate the QD. Most organic surfactants have frontier orbitals with energies that are far from resonant with the semiconductor band edges and therefore present potential barriers on the order of several electron volts; these barriers

confine the electron and hole density to the inorganic core. The frontier orbitals of certain organic ligands, however, have
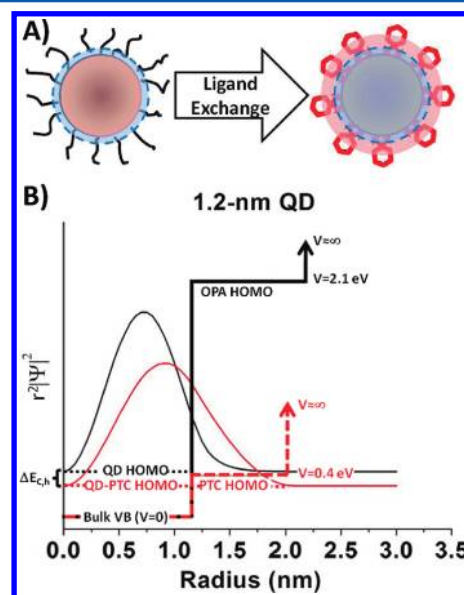

Figure 1. (A) The electron (blue) and hole (pink) wave functions are sensitive to the electronic structure of the surfactant. Native aliphatic ligands (black) are replaced with phenyldithiocarbamate, PTC (red), which has the proper energetic and spatial alignment to interact selectively with the excitonic hole. (B) Example wave function for an excitonic hole in 1.2 nm CdSe QDs with native octylphosphonic acid (OPA) ligands (black) and after PTC exchange (red). The energy of the excitonic hole is decreased, and the hole density extends farther into the surfactant to the organic−solvent interface after PTC exchange. The increased density of the hole wave function in the surfactant upon PTC adsorption results in up to a 1 eV reduction in confinement energy for the exciton. Reprinted with permission from ref 11. Copyright 2011 American Chemical Society.

appropriate energetic and spatial alignment to mix with the orbitals of the QD and thus determine the energies and electron distributions not only of local surface states but also of the delocalized excitonic state formed upon photoexcitation of the QD. These ligands blur the boundary of the heterogeneous interface by drawing a significant portion of the carrier wave function into the organic surfactant layer, Figure 1A.

We have identified an organic ligand, phenyldithiocarbamate (PTC), that induces dramatic bathochromic (red) shifts (up to 1 eV) in the grand-state absorption spectra of colloidal QDs.[10,11] The HOMO of PTC has the correct energetic alignment and spatial symmetry to strongly mix with the valence band edge states of common QD materials; this orbital mixing decreases the confinement energy of the exciton through a reduction in the height of the tunneling barrier presented to the hole at the organic−inorganic interface (Figure 1B). We observe reductions in the energy of the optical band gap of CdS QDs, for example, of up to 1 eV. This delocalization effect is dramatically larger than that of thiols, which have frontier orbitals that align with semiconductor band edges only slightly better than those of other common surfactants such as phosphonates and carboxylates; therefore, their perturbation to the ground-state spectra of QDs is small (1 to ∼50 meV).[12,13]

The energetic resonance of the HOMO of PTC with the valence band edges of CdSe, CdS, and PbS QDs and the lack of resonance of the LUMO of PTC with the conduction band
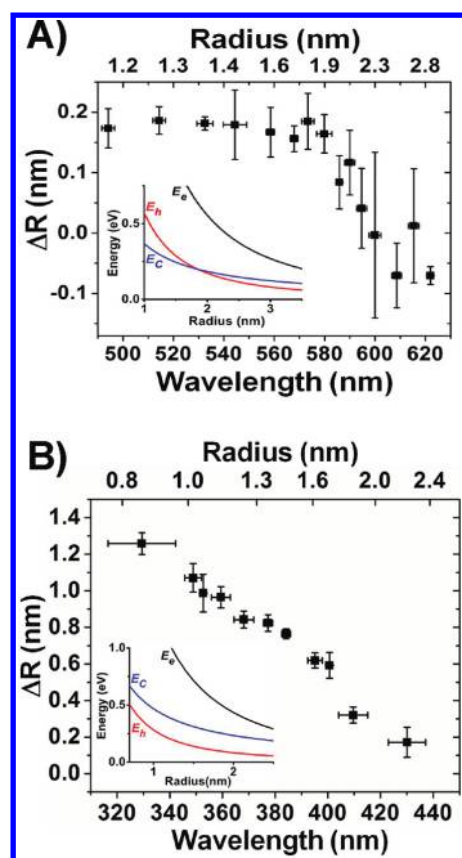
Figure 2. Plots of ΔR (a measure of PTC-induced relaxation of confinement) as a function of the wavelength of the first absorption maximum (bottom axes) and QD radius (top axes) for (A) CdSe and (B) CdS. The insets show the calculated Coulomb (blue), electron (black), and hole (red) confinement energies. The transition from strong to intermediate confinement occurs when the attractive Coulomb energy becomes larger than the kinetic confinement energy. Reprinted with permission from ref 11. Copyright 2011 American Chemical Society.

edges of these materials suggest that PTC should act selectively on the wave function of the hole.[11] We have extensive evidence of the carrier selectivity of PTC-induced delocalization. Figure 2 shows plots of the effective delocalization radius ΔR observed upon PTC adsorption as a function of the physical radius of the QD (R) for CdSe and CdS. In both cases, the asymmetry of the electronic structures of the electron and hole leads to different dependencies of the confinement energy on R for those carriers. For CdSe and CdS, the excitonic electron is strongly confined over the entire range of sizes of QDs that we studied, where "strong" confinement requires that the confinement energy for the carrier be larger than the exciton binding energy for the electron−hole pair (see insets). The observation that the effect of PTC on the optical band gap of the QDs goes to 0 (i.e., ΔR = 0) in the regime of strong confinement for the electron indicates that the electron is not participating in the exciton delocalization and that the PTC interaction is hole-specific. The observed carrier specificity of the PTC interaction confirmed our hypothesis that energetic alignment of the frontier orbitals of the QD and the ligand primarily determines the magnitude of orbital mixing at the interface. We suspect that this specificity applies also to PbS but cannot prove it from the ΔR plot because the electron and hole in PbS have parallel

electronic structures and therefore nearly identical effective masses.

The transition from strong to intermediate confinement of the hole is apparent in the ΔR plot for CdSe as the radius at which the PTC-induced delocalization begins to diminish (∼1.9 nm). This radius is also that at which the Coulomb binding energy for the electron−hole pair (which goes as $1/R$)[14] and the confinement energy for the hole (which goes as $1/R^2$ for a particle in a spherical potential well)[14] contribute approximately equally to the total energy of the carrier.

Our next goal is to adjust the alignment between QD band edges and PTC frontier orbitals (possibly achieving even larger shifts in the QD absorption spectrum) through substitution of the phenyl ring within PTC at the para position with electron-donating and -withdrawing groups. This strategy may also serve to identify precisely the position of the valence band edge of CdSe and CdS QDs, a quantity that is difficult to measure electrochemically or predict with electronic structure calculations.

> We suspect that dithiocarbamates are one of many classes of molecules that have the correct orbital energies and symmetry to cause large changes in confinement energies of excitonic carriers.

From a technological perspective, the most interesting potential use of QDs treated with PTC or other strongly interacting ligands is enhancement of carrier-specific modes of conductivity in QD films. Selective delocalization of hole wave functions, for example, will, in principle, increase the electronic coupling among the valence bands of QDs within a film and selectively enhance hole mobilities. Conjugated dithiocarbamates, along with ligands with specific electron-delocalizing properties, would provide a toolbox for designing QD films with electron and hole mobilities that are selectively tunable through the size, material, and surface functionalization.

It is useful to compare the effect of PTC on QDs to that of electroactive ligands on the absorption spectra of metal oxide nanoparticles. In many dispersed and solid-state nanocrystalline TiO_2 systems, adsorption of electron-donating ligands (most prominently enediols, mercaptocarboxylic acids, and calixarenes) to undercoordinated (electron-deficient) titanium sites results in charge-transfer NP−ligand interactions in the ground state.[15−19] These local interactions induce new transitions (ligand-to-metal charge transfer or LMCT transitions) that are often red-shifted from the band gap of the semiconductor particle itself and therefore create absorption features in the visible region that are useful for photosensitization. This interaction is facilitated by bidentate binding, often through a carboxylate group. A local CT interaction such as those in metal oxide NPs between the sulfurs of PTC and the Cd^{2+} to which it binds almost certainly occurs. In the QD−PTC system, however, it is not the additive effect of these local CT interactions that induces a new, red-shifted absorption in the QD spectrum. In this system, the local interactions facilitate

subsequent coupling of the QD excited state with the ground state of the PTC through a lowering of the tunneling barrier for the wave function of the excitonic hole at the inorganic–organic interface. The summative effect of the local QD–PTC interactions is therefore a reduction in the confinement energy of the exciton (and therefore a uniform shift of all features in the excitonic spectrum) rather than creation of new, red-shifted absorptions.

Changes in the shape of the excitonic wave function induced by PTC affect the spatial overlap of the electron and hole and therefore the rate and yield of radiative decay (an interesting problem that we are currently investigating). The most common strategy for changing the photoluminescence (PL) quantum yield using organic ligands, however, is to change the degree of passivation of local surface states that, when unpassivated, are thermodynamic traps for excitonic charge carriers.

Carrier-Resolved Analysis of Ligand-Mediated Exciton Decay Pathways. Charge trapping is a process by which the electron or hole is transferred from its initial delocalized excitonic state to a state localized within the core lattice of the QD (lattice trap)[20] or on a surface atom (surface trap).[3] Ligands influence the rates of surface-trapping processes by donating electron or hole density that raises or lowers the energy of a localized trap state.[21] The resulting state, which may or may not remain a trap state with an energy that lies within the band gap of the QD, has a mixed character (QD and ligand). Passivation schemes attempt to increase the probability for radiative decay by decreasing the availability and/or efficiency of nonradiative decay pathways for the exciton, but not all organic ligands serve as effective passivators; some, such as substituted anilines,[21] do not perturb trap state energies enough to move them outside of the band gap, and some, such as thiol ligands, actually create new trap states.[3,22] The sensitivity of the decay of the exciton to organic ligands provides an opportunity to control the dynamics and fate of the exciton by controlling the properties of these ligands; however, in order to achieve ligand-mediated control of the excitonic charge carriers, we need to understand the specific mechanisms by which ligands affect the PL efficiency of QDs.

> The sensitivity of the decay of the exciton to organic ligands provides an opportunity to control the dynamics and fate of the exciton by controlling the properties of these ligands.

Processes that remove photoexcited charge carriers from band edge states and lead to nonradiative decay (recombination) of the exciton generally involve either the electron or the hole, but not both. Complete mechanistic analysis of the decay process requires identification of the responsible carrier. One useful method for distinguishing electron- from hole-mediated decay pathways is transient absorption (TA) spectroscopy of solutions of QDs and organic ligands. Figure 3 contains a
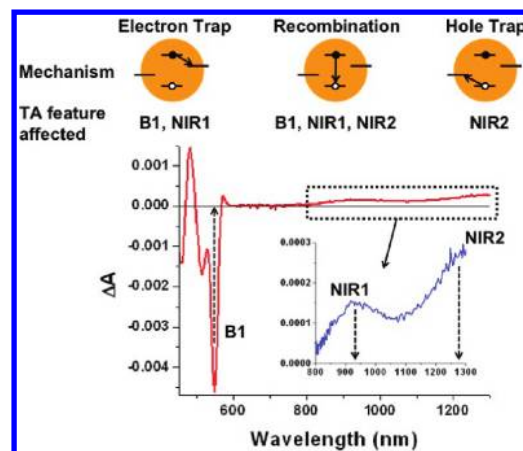

Figure 3. (Bottom) Differential absorption spectrum of a solution of CdSe QDs in CCl_4 500 fs after excitation at the first absorption feature (550 nm; data adapted from ref 23). The feature labeled B1 corresponds to the bleach of the first absorption feature, and the features labeled NIR1 and NIR2 (inset) correspond to intraband absorptions of the electron and the hole. The dotted arrows indicate how the amplitudes of these features change as the delay between the pump and probe pulses increases. (Top) The cartoons illustrate mechanisms of excitonic decay and the absorption features that they affect. The black circles denote electrons, and the white circles denote holes.

representative transient absorption spectrum of a solution of CdSe QDs 500 fs after excitation to their lowest-energy (band edge) excited state.[23] The feature labeled B1 is the bleach of the lowest-energy ground-state absorption feature. For CdSe and CdS QDs, the amplitude of the B1 feature reflects the population of electrons in the lowest-energy conduction band state ($1S_e$ state) and is not sensitive to the presence of holes in the valence band.[20,24] The absorption features in the near-infrared (NIR, labeled NIR1 and NIR2) are due to overlapping intraband absorptions of the electron and hole. The higher-energy absorptions (NIR1) are mostly due to transitions of the electron from the $1S_e$ state to higher-energy conduction band states, and the lower-energy absorptions (NIR2) are mostly due to transitions of the hole from the valence band edge ($1S_{3/2}$ state) to lower-energy valence band states.[23,25] A process that removes electrons from the conduction band, such as electron trapping, decreases the amplitudes of B1 and NIR1 but will have less of an effect on NIR2. Similarly, a process that removes holes from the valence band, such as hole trapping, decreases the amplitude of NIR2 but has a minimal effect on B1 and NIR1. A process that removes both electrons and holes from the conduction and valence bands, such as radiative recombination, decreases the amplitudes of all three features.

The dynamics with which the features in a TA spectrum of QDs decay are often multiexponential due to the heterogeneity of the sample as well as contributions from consecutive decay processes. Comparison of the time constants and amplitudes of the multiexponential decays of the electron-specific features with those of the hole-specific features allows the contributions of electron and hole processes to each exponential decay component to be quantified and enables the subsequent assignment of the mechanisms associated with these decay components.[26] Furthermore, the effect of an added ligand on the dynamics of charge-carrier-specific features can help determine whether the ligand interacts with the electron or the hole. For example, for CdSe, a ligand such as benzoquinone
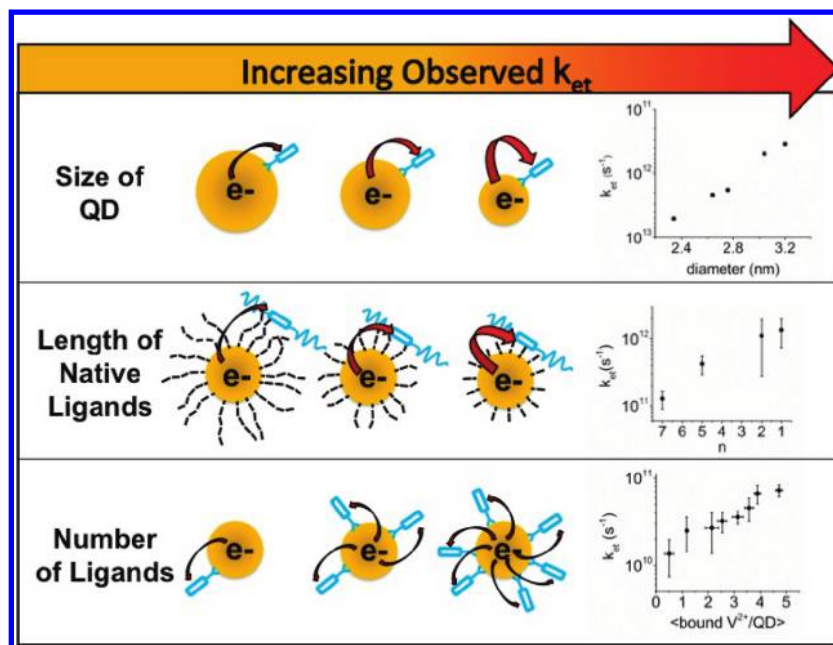
Figure 4. Schematic diagram illustrating three parameters within QD−ligand complexes that have been shown to affect the observed rate of the electron-transfer process (k_{et}). In each series, k_{et} increases from left to right. (Top): Decreasing the size of the QD increases k_{et} by increasing the driving force for the electron-transfer reaction. (Top, inset): Plot of k_{et} as a function of the diameter of the QD for CdSe QD−methyl viologen complexes in CHCl$_3$. (Middle): Decreasing the length of the native ligands through which the electron must tunnel when the redox-active ligand is sterically hindered and cannot penetrate the ligand shell increases k_{et}. (Middle, inset): Plot of k_{et} for poly(viologen)/CdSe films as a function of n, the number of methylene groups in the native ligands that form the spacers between the donor and acceptor. These data are adapted from ref 38. (Bottom): Increasing the number surface-bound ligands increases k_{et} by increasing the number of pathways by which electron transfer can occur. (Bottom, inset): Plot of k_{et} for CdS QD-N-[1-heptyl],N'-[3-carboxypropyl]-4,4'-bipyridinium (V^{2+}) dihexafluorophosphate complexes in dicholoromethane as a function of the mean number of adsorbed V^{2+}/QD. These data are adapted from ref 27.

that affects the dynamics of B1 and NIR1 but not NIR2 interacts predominantly with the electron, whereas a ligand such as octanethiol that affects the dynamics of NIR2 interacts predominantly with the hole.[23]

It can be difficult to determine whether a ligand quenches the PL of a QD by increasing the number or efficiency of charge-trapping states or by participating in charge transfer, which involves the complete transfer of the electron (or hole) from the excited state of the QD to a state that lies entirely on the ligand and results in a reduced (or oxidized) ligand and an oxidized (or reduced) QD. In some cases, observation of an absorption feature from a radical anion or cation of the ligand in the TA spectrum enables the easy identification of an electron- or hole-transfer mechanism for PL quenching,[27,28] but often, the features are buried under the QD spectrum. In that case, we must rely on comparisons of the dynamics of the QD excited states with and without the ligand present to deduce the presence of a charge-transfer pathway. Inspection of carrier-specific features in the TA spectrum, along with estimates of driving forces for charge transfer, is extremely useful in eliminating or supporting charge transfer as the mechanism by which a ligand quenches the PL of QDs.

Role of Heterogeneity in the Rates of Interfacial Charge Transfer for QD−Ligand Complexes. Many proposed applications of QDs necessitate the transmission of charge into and out of the QD. Ligands bound to the surface of the QD can be used to regulate the rates of charge injection and charge extraction. Developing a mechanistic understanding of how the chemical and structural properties at the QD−ligand interface influence these electron-transfer rates is a major challenge in gaining control over these processes. To understand this relationship, we need to correlate

changes in the chemical structure and composition of the QD−ligand interface to changes in the interfacial electron-transfer rate constant. Some progress has been made toward this end,[29,30] but efforts have largely been limited by the heterogeneity of these systems and the difficulty in quantifying and characterizing the chemical structure and composition of the QD−ligand interface.

Previous studies of charge dynamics in QD−ligand complexes have primarily sought to explain the observed trends in the charge-transfer rate within the context of Marcus theory.[31−33] Several groups have found that decreasing the size of the QD (and thereby increasing the confinement energy of the charge carriers) increases the rate of electron transfer due to the increased driving force for the photoinduced electron transfer (PET) reaction (Figure 4). All of these studies have found a Marcus-normal relationship between the driving force and rate of the PET reaction,[32,34,35] and there have been no reports as of yet of the inverted region in these systems. It is noteworthy that the majority of these studies have measured the charge separation process, and much less research has been directed toward charge recombination.[36] Apart from the well-studied size dependence of the charge-transfer rate, other studies have shown that increasing the distance between the QD core and the charge-accepting partner, either by growing an inorganic shell on the QD[37] or adding longer insulating ligands,[30,38] decreases the PET rate (Figure 4).

Ostensibly, measuring PET rates in QD−ligand complexes is completely analogous to PET measurements in intra- and intermolecular ET systems that are readily addressed with an accessible suite of time-resolved spectroscopies (primarily TA and time-resolved photoluminescence). Solutions of QD−ligand

complexes are inherently heterogeneous in multiple parameters, three of which are illustrated in Figure 4, that directly influence the charge-transfer process, including (i) the size and shape of QDs, (ii) the type and number of surface-bound ligands per QD, (iii) the conformation of the ligand on the surface of the QD, (iv) the dynamic exchange of surface-bound and free ligands, and (v) the structure and composition of the surface atoms on the QD. In light of this heterogeneity, the PET rate constant that we measure for a particular sample of QD−ligand complexes is an average of a distribution of rate constants that reflects an ensemble that is heterogeneous with respect to all of the parameters listed above. Each plot in Figure 4, therefore, shows average PET rates for various ensembles of QD−ligand complexes for which one particular parameter—the average QD diameter, length of the native ligand, or average number of bound ligands—has been varied systematically.

The observed PET rate in QD−ligand complexes is linearly proportional to the number of surface-bound ligands per QD (Figure 4).[27,28] Not every QD within an ensemble contains the same number of surface-bound ligands. Measuring the intrinsic PET rate (k_{int}, the rate for a single QD−ligand pair), therefore, requires measuring the number of surface-bound ligands per QD. We, and others, have successfully implemented a model developed by Tachiya to describe the distributed PET dynamics in QD−ligand systems.[27,39] Tachiya's model employs either the binomial distribution or the Poisson distribution (depending on the degree of saturation of the QD surface[40]) to describe the distribution of the number of surface-bound ligands per QD and then fits the electron-transfer rates to a sum of exponentials, where the prefactor for each exponential function corresponds to the probability of finding a QD with m surface-bound ligands (as predicted by the Poisson or binomial distribution).[41] We use the amplitude of the QD bleach feature in the TA spectrum of CdS QD−viologen complexes as a measure of the probability of finding a QD with zero bound ligands and, from this probability, infer the distribution of surface-bound ligands in the ensemble.[27] This type of analysis allows us to calculate the adsorption constant, K_a, for the QD−viologen complex and to extract a value for the nondistributed PET rate constant, k_{int}, within a heterogeneous ensemble. Lian and co-workers have verified the validity of the Poisson distribution in describing the number of surface-bound ligands per QD by constructing histograms of PET rates from single-particle measurements of PET from QDs to adsorbed fullerene molecules.[39]

Measurements of PET rate constants in QD−ligand systems are usually complicated, however, by the complex, nonexponential PET dynamics due to heterogeneity within the QD−ligand ensembles.

There are several sources of heterogeneity in solution-phase QD−ligand complexes that are yet to be accounted for in analyzing PET dynamics. (i) Fritzinger et al.[42] have shown that the ligands in QD−ligand complexes are in dynamic equilibrium between bound and free states. This result implies that, under certain circumstances, there exists a combination of static and dynamic electron-transfer processes. (ii) Jones et al.[43] have modeled the distribution of surface states within the band gap of CdSe QDs to explain the temperature dependence of observed charge-trapping rates. If these trap states, rather than the band edge exciton, serve as the direct precursor to the radical ion pair state, then the heterogeneity of these states, that is, the distribution of energy gaps and couplings between the trap states and the charge-separated states, should appear in the model for the PET rate. (iii) There are often multiple potential binding geometries for ligands on the QD surface, and each conformation may lead to its own magnitude of donor−acceptor electronic coupling and therefore its own PET rate. Inclusion of this type of heterogeneity in PET analysis requires quantitative measurements of the binding geometries of ligands on QD surfaces. This type of information is difficult to obtain from traditional analytical techniques applied to solution-phase QD−ligand samples because the signals (NMR, electronic absorptions, vibrational absorptions) from surface-bound ligands are often highly convoluted with those from free ligands. The complexity of the QD−ligand interface presents many opportunities for constructing a model for QD−ligand electron transfer that is as predictive as Marcus Theory has been for electron transfer in molecules.

Ongoing Work and Future Directions: Direct Measurements of Nonradiative Dissipation of the Exciton. Even with the extensive amount of work on the population decay pathways of excitonic charge carriers within QDs, the forces that direct charge carriers in nonradiative dissipation pathways are not precisely described. As highlighted earlier, the experimental observations of fast cooling times that contradict the theoretically predicted phonon bottleneck[5,20,44,45] and the still-debated mechanism for the transient "off-states" in the blinking trajectory of QDs illustrate how the shape[46] and surface composition[47] of QDs contribute to their electronic structure and thus to the available decay pathways for individual charge carriers. Nonlinear optical spectroscopies are useful tools for determining the correlation between structure and exciton dynamics by providing means to either selectively probe the surface structure with three-wave mixing techniques[48] or to directly measure dissipative pathways within the QD using four-wave mixing (FWM) techniques.

FWM techniques involve three spatially and temporally overlapped laser pulses in a sample with a fixed geometry, where phase-matching conditions result in scattering of the input photons and the output of a fourth wave in predetermined directions. By tuning the energy differences between the input beams and their phase-matching conditions, a variety of experiments—transient population gratings, photon echo, and coherent Raman spectroscopies—are possible. These experiments provide information beyond population dynamics, such as the electronic and/or vibrational coherences that exist within the sample, the lifetimes of these coherences, and the contribution of heterogeneous and homogeneous components to spectral line widths and to the decoherence of a given signal. Photon echo experiments dominate the existing work on colloidal systems. They provide information on dephasing times associated with the acoustic and optical phonon modes as a function of size,[49] temperature,[50] and lattice matching between the core and various inorganic shells[51] and have demonstrated electronic coherences within biexcitons.[52]

The observation that the capping structure of a QD impacts the dephasing times of phonon modes reinforces the

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importance of the QD surface in energy dissipation, but no FWM experiments to date directly investigate the organic ligands that cap the surface of the QD. One particular time-resolved FWM technique, coherent antistokes Raman spectroscopy (CARS), is especially appropriate for probing the magnitude and lifetime of coupling of excitons to ligand vibrations, surface modes, and core phonons. If a ligand is coupled to either excitonic creation or decay mechanisms, one would expect to see an effective "resonance" enhancement of the mode as energy is exchanged with this mode. By measuring the temporal profile of the intensity modulation of specific ligand modes after photoexcitation of an ensemble of QDs, one can determine what ligands are involved in excitonic dissipation and can compare lifetimes of electron–phonon interactions to time constants for decay of excitonic charge carriers obtained with linear spectroscopies.[20] A map of the chemical origins of exciton decay will allow one to tune the optical properties of the QDs by tuning their surface chemistry.

Finally, in considering the potential of QDs to act as light-harvesting and charge-transport materials within photovoltaic, photocatalytic, sensing, or light-emitting devices, it is important to determine the properties of QD surfaces under prolonged excitation. Specifically, surface charging has been implicated in changes in ultrafast dynamics and photobrightening of QDs[53] and in blinking phenomena that appear to be ubiquitous in quantum-confined semiconductors. Theoretical[54] and experimental[55] consensus is building that the previous model implicating Auger recombination with a delocalized core charge cannot account for the off-state in QD blinking trajectories (states competing with Auger recombination are still emissive[56]) and that the *localized* surface charges[54] and multiple charging[57] events result in the shutdown of emission. Interestingly, others[58–60] have demonstrated that electron–phonon coupling increases by up to 4 orders of magnitude upon charging of the QD. Further experiments investigating both the nature of the trapped charges (hole or electron, surface, or core) and the resulting modifications to energy dissipation pathways may help to elucidate the mechanism(s) that dictates blinking trajectories. Nonblinking QDs materials are useful in applications from laser gain media and single-photon light sources for nanophotonic devices to widely tunable and highly efficient LEDs and light-harvesting materials for solar energy conversion.

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Biographies
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