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early stage researchers
workshop
in nanoscience



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14th early stage researchers workshop in nanoscience



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Programme

8:45 Reception

9:15 Welcome

Prof. Rodolfo Miranda

IMDEA Nanociencia Director

9:30 Invited talk

Prof. Pablo Ares

Universidad Autónoma de Madrid

Advanced atomic force microscopy: a tool for nanoscience and nanotechnology

SESSION 1

Chair: Allan S. Johnson

10:15 Roberto Sánchez Institut Català de Nanociència i Nanotecnologia (ICN2)

Ozone-mediated selective bond cleavage in covalent organic frameworks

10:30 Pablo Martínez

Universidad Autónoma de Madrid

Ballistic-diffusive crossover in single-molecule heat transport

10:45 Peijiang Wang Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC)

The role of temperature in the photoluminescence quantum yield of Ag₂S-based nanocrystals

11:00 Miguel Varea

IMDEA Nanociencia

Light-matter interaction of field emission resonances in a scanning tunneling microscope

11:15 Coffee break / POSTER SESSION 1

12:00 Invited talk

Dr. María Sancho

Universidad de Zaragoza

Hybrid vectors involving extracellular vesicles and nanoparticles for cancer treatment and diagnosis

SESSION 2

Chair: Gloria Tobajas

12:45 Sara Gullace

IMDEA Nanociencia

Room-temperature laser induced water release in a spin-crossover metal-organic framework: a structure-properties investigation

13:00 Rosalia López

IMDEA Nanociencia

Plasmonic nanoparticle-mediated photothermia: nanothermometric temperatures and cellular-level thermal effects

13:15 Patricia Izquierdo

Universidad Complutense de Madrid

Molecular bilayer nanographenes: the search for enantioselectivity

13:30 M. Carmen González

IMDEA Nanociencia

Exploring bacterial-surface interactions with a fluorescent membrane tension probe

13:45 Lunch

14:45 POSTER SESSION 2

SESSION 3

Chair: Alberto Martín

15:30 **Julia García**
IMDEA Nanociencia

Cavity optomechanics in MoS₂ micro-drum resonators

15:45 **Esther González** Centro Nacional de Biotecnología (CNB-CSIC)
Super-resolution microscopy reveals how viral infection reshapes host genome structure by sequestering RNAP II

16:00 **Mario Martínez**
IMDEA Nanociencia

Multifunctionalized gold nanoparticles for biomedical applications

16:15 **Raúl Solís**
IMDEA Nanociencia

Implementation of spin-orbit torque biasing into manganite AMR sensors

16:30 **Coffee break / POSTER SESSION 3**

SESSION 4

Chair: Luis A. Campos

17:00 **Luis Calahorra**
IMDEA Nanociencia / IQOG-CSIC

Lipopeptides as tools to mimic life-like behaviour

17:15 **Rafael Delgado**
Universidad de Castilla-La Mancha

Magnetometry study of a corrugated magnetic thin film with stable antiparallel domains

17:30 **Daniel García**
Universidad Autónoma de Madrid

Innovative COF-based biosensor for autism spectrum disorder biomarker detection

17:45 **Indranil Bhattacharjee**
IMDEA Nanociencia

1,6-diazapyprene: a model nitrogen-doped polycyclic aromatic hydrocarbon molecule for spectroscopic and quantum mechanical analysis

18:00 **Closing remarks and awards**

Plenary Lectures



Plenary Lectures



Advanced atomic force microscopy: a tool for nanoscience and nanotechnology

Abstract

Scanning Probe Microscopy (SPM) techniques (STM, AFM, SNOM...) have been crucial for the emergence of Nanoscience and Nanotechnology. These fields represent new frontiers to study a variety of physical, chemical and biological phenomena on a scale at least 10000 times smaller than the world we normally observe. In this talk, I will present my research of the last years on low dimensional systems through the use and development of advanced Atomic force Microscopy (AFM) tools. I will start with a brief introduction on instrumental and methodological contributions to the advancement of nanoscale characterization techniques, including a novel and simple method to fabricate nanoelectrodes by AFM manipulation and assembly of metal nanowires. Then I will comment the work done on tuning graphene properties by applying ultrahigh pressures locally, along with the isolation of antimonene, one of the few elementary 2D allotropes. I will go on showing the electrical characterization of different low dimensional systems: long molecular wires, and ultrathin hexagonal Boron Nitride (hBN) layers.

Biography

Pablo Ares completed his studies in Physics at the Universidad Complutense de Madrid in 2003, and then joined Nanotec Electrónica S.L. (a company devoted to the design, development and commercialization of scanning probe microscopes, SPMs) as an Application Scientist. In 2014, he moved to the Department of Condensed Matter Physics at the Universidad Autónoma de Madrid (UAM), where he obtained his Ph.D. in 2017. He then joined the Graphene Group at the University of Manchester (UK), where he worked with Prof. Kostya Novoselov and Dr. Laura Fumagalli as a Marie Skłodowska Curie Fellow. In 2020, he returned to the UAM as an Assistant Professor & IFIMAC Junior Leader, where he is currently a Ramón y Cajal Fellow since 2022. He has obtained national and international competitive funding, including a prestigious ERC Starting Grant 2024 for his project (HeaT2Defects). His research activity has a strong multidisciplinary character within the framework of nanoscience and nanotechnology, focusing on novel low-dimensional systems, with particular attention to 2D materials, using and developing SPM tools.



Hybrid vectors involving extracellular vesicles and nanoparticles for cancer treatment and diagnosis

Abstract

Cancer is a multifaceted global health issue that continues to demand new solutions. The advent of nanotechnology has added nanoparticle (NPs)-based approaches to the available toolbox in cancer therapy and diagnosis. Indeed, there are now nanosystems with extraordinary properties, including drug loading, antibody functionalization, imaging agents and remote activation capabilities. However, these promising advances have so far failed to materialize in the clinic, largely due to a lack of selective delivery to tumors. Nanomedicine was heralded as the solution to this lack of the treatment efficacy against cancer. But, the delivery of therapeutic nanoparticles (NPs) to cancer sites needs to be dramatically improved. In the last years, the "Trojan Horse" concept has been postulated as an emerging strategy for enhancing tumor targeting efficiency. Among "Trojan Horse" strategies, extracellular vesicles (EVs) appear to hold the greatest potential as tools for the solution of the targeting challenge. They are nanovesicles (50-120 nm of diameter) from endocytic nature secreted by almost all cell types. In this communication, I will present an overview of the combination of multidisciplinary approaches based on the latest advances in the field of nanomedicine and in the area of the EVs for efficiently loading EVs with therapeutic NPs (for instance with optical hyperthermia properties or with bioorthogonal catalytic activity) or imaging agents, and selectively delivering them to target tumor sites. I will present some of the last novel strategies developed for the encapsulation and engineering of therapeutic nanotechnological materials within EVs and their application for cancer treatment and diagnosis.

Biography

BSc in Biotechnology (2015), MSc in Nanostructured Materials (2016) and PhD in Chemical Engineering by the University of Zaragoza (2020) holding a predoctoral FPU fellowship from the Spanish Ministry of Education. During her PhD she joined the groups of Prof. Andrew De Mello (ETH Zurich) and of Prof. Pierangelo Metrangolo (University of Milan). In 2021 she moved to the Mario Negri Institute (Milan), joining the group of Prof. Luisa De Cola as postdoctoral researcher where she was granted with a two-year AIRC-for Italy fellowship focused on the design of breakable on demand and stimuli-responsive organosilica NPs for biomedical applications. In 2023, she obtained a prestigious Postdoctoral AECC Talent Fellowship and moved back to Spain to the NFP group led by Prof. Jesús Santamaría, part of INMA from the University of Zaragoza. In 2024, she gained a Marie Skłodowska Curie Individual Fellowship that will start in the following year. Main current research lines: 1) the combination of nanostructured materials, molecular biology and biochemistry with physicochemical, microfluidics and nanotechnological techniques in the field of extracellular vesicles; and in 2) the development of novel selective nanoscaled-drug delivery tools for cancer treatment and diagnosis.

Oral Communications



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- 2 Pablo Martínez *Universidad Autónoma de Madrid*
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- 3 Peijiang Wang *Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC)*
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- 4 Miguel Varea *IMDEA Nanociencia*
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1,6-diazapyrene: a model nitrogen-doped polyaromatic hydrocarbon molecule for spectroscopic and quantum mechanical analysis

OZONE-MEDIATED SELECTIVE BOND CLEAVAGE IN COVALENT ORGANIC FRAMEWORKS

Roberto Sánchez-Naya,^{*ab} Juan Pablo Cavalieri,^{abc} Jorge Albalad,^{ab} Inhar Imaz^{ab} and Daniel Maspoch^{abd}

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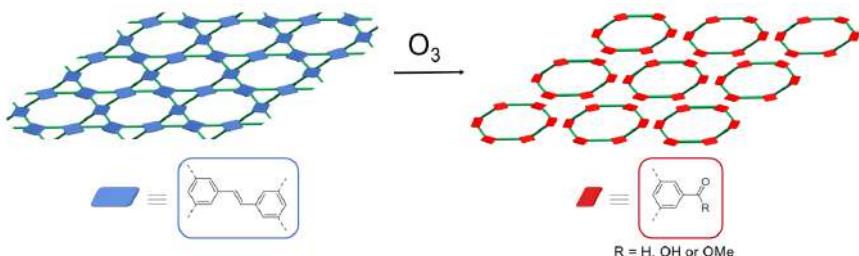
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The implementation of bond breaking is a useful tool in chemical synthesis for obtaining new molecules and materials. By employing ozone gas as a successful trigger for this transformation, control at the molecular level via selective ozonolysis can be achieved. Recently, we have introduced the concept of Clip-off Chemistry as a new synthetic methodology based on the specific bond cleavage of reticular materials composed of molecular building blocks that present moieties susceptible to be broken, e.g., olefin bonds via ozonolysis. This selective, quantitative and periodic bond breaking results in spatial control of the disassembly process and enables the formation of new molecules and materials.¹

As structures analogous to MOFs, covalent organic frameworks (COFs) are reticular materials based on purely organic building blocks linked by strong covalent bonds. COFs offer a platform for the incorporation of a wide variety of molecules to cover a vast range of applications, such as photocatalysis, organic electronics, gas adsorption and environmental remediation, among others.² In this work, we attempt to extend the concept of Clip-off Chemistry to the organic scaffold of COFs. We will present the effect of the ozone on the COF linkages for the implementation of non ozonizable bonds. Also, we will show that the control of the topology and the location of the regions susceptible to the cleavage may lead to the controlled disassembly of COFs into defined discrete molecules.



Scheme 1. Schematic representation of Clip-off Chemistry in a two-dimensional COF layer.

Notes and References

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Ballistic-Diffusive Crossover in Single-Molecule Heat Transport

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Understanding and controlling heat transport at the nanoscale is arguably one of the largest pending challenges of Nanoscience. The field has witnessed a renewed interest with recent spectacular experiments including measuring heat transport through a single-atom contacts, then through a single molecule junctions¹ and later the realization of the first molecular-sized nano-refrigerator. However, a fundamental understanding of the novel and exotic heat transport phenomena at these scales remains elusive, ultimately hindering a de-novo design of novel nano-materials with tailored heat transport properties.

In this work, we performed advanced all-atom non-equilibrium simulations to achieve atomically detailed insights into heat transport in benchmark single-molecule alkanes ranging from few atoms up to 2 micrometer long chains. Our simulations, quantitatively reproduce experimental data¹, but most importantly they provide an atomically detailed understanding on the breakdown of Fourier's classical law for heat transport as new a form of coherent heat transport emerges (ballistic) and how its transition towards the classical limit showcases abnormal, global thermalization for all phonon modes in the chain. Spectral decomposition of heat flux² unveils the non-local nature of this phenomenon thus paving the road for chemically engineering heat transport at the nanoscale.

Alternatively, we also explore how tensile strain affects the crossover between both transport regimes (ballistic or diffusive) and overall conductance of alkane chains. By focusing on a relatively simple system, we gain valuable insights into the fundamental factors governing heat transport at the nanoscale.



FIGURE: Sample geometry for a 32-unit alkane chain between two gold reservoirs. The temperature difference between electrodes drives a heat flux through the molecular wire.

Notes and References

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The role of temperature in the photoluminescence quantum yield (PLQY) of Ag₂S-based nanocrystals

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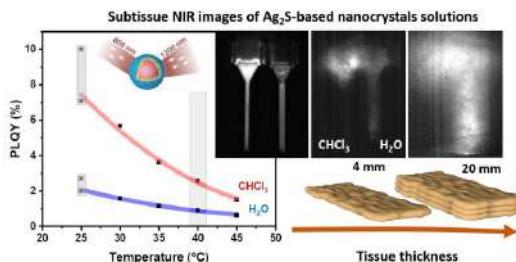
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A method for synthesizing Ag₂(S,Se)@ZnS nanocrystals (NCs) with high near-infrared emission performance via a simple hot injection process has been reported. The photoluminescence quantum yield (PLQY) in organic solvents can reach up to 10%, significantly higher than untreated Ag₂S ones. The temperature-dependent PLQY of Ag₂(S,Se)@ZnS NCs in both organic and aqueous media was qualitatively analyzed. As temperature increases, the PLQY of the nanocrystals in both media decreases significantly, but the nanocrystals in water exhibited better thermal stability. Based on the temperature-dependent PLQY properties of Ag₂(S,Se)@ZnS NCs, their thermal sensitivity (approximately 2.5%/°C) in the physiological temperature range was studied. Additionally, their NIR penetration performance through 20 mm thick tissue was further explored with hyperspectral imaging, demonstrating that surface-passivated Ag₂(S,Se)@ZnS NCs exhibit enhanced imaging clarity and deep tissue penetration capability. These findings provide new design approaches and evaluation standards for their applications in NIR imaging and luminescence nanothermometry.¹



Left: PLQY variation with temperature for Ag₂(S,Se)@ZnS NCs in chloroform and water. Right: hyperspectral images of cuvettes containing Ag₂(S,Se)@ZnS NC solutions in chloroform and water. The cuvettes were covered with 4 and 20 mm thick tissues, as schematically depicted.

Notes and References

- Wang, P. et al. The role of temperature in the photoluminescence quantum yield (PLQY) of Ag₂S-based nanocrystals. *Mater. Horiz.* (2024) doi:10.1039/D4MH01016G.

Light-matter interaction of field emission resonances in a scanning tunneling microscope

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The combination of scanning tunneling microscopy with laser light offers the unique possibility to investigate and control light-matter interaction at the atomic scale, which is critical for the development of novel technologies from diverse branches, such as quantum computing, optoelectronics, sensing, or catalysis, to mention a few. In our work, we investigate the effect of continuous wave (CW) laser illumination on the field emission resonances (FER) formed between a gold tip and a Ag sample by measuring the derivative of the tunneling current as a function of the bias voltage. It was previously reported that the effect of CW illumination was that the lowest energy FER downshifts by the photon energy, being the hallmark of plasmon-assisted resonant tunneling [1]. We have extended these investigations and made a thorough experimental characterization of the effects induced by the laser power, tunneling current, and polarization of the excitation laser on the FERs. Interestingly, several peaks in the FER spectra appear/disappear upon laser illumination when varying polarization, laser power, or tunneling current, whose positions and intensities follow a non-trivial dependence. Our observations cannot be described only assuming plasmon-assisted resonant tunneling, indicating that the strong field confinement of the laser fields due to the tip-sample nanocavity may be responsible for the observed effects.

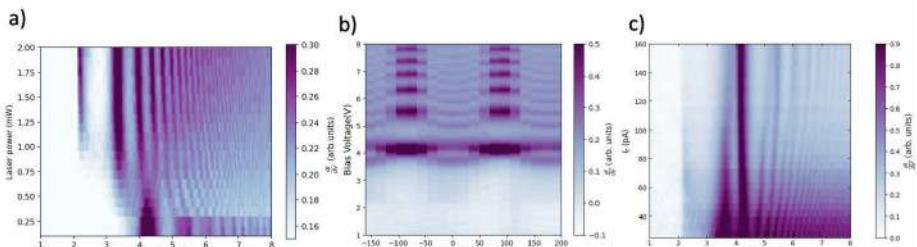


Fig 1: FER dependence on: a) Laser power, b) Laser's polarization direction and c) Tunnel current set-point. These three graphs show a color map of how the differential conductance curves evolve with the change in the previously mentioned parameters.

Notes and References

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Room-Temperature Laser Induced Water Release in a Spin-Crossover Metal-Organic Framework: a Structure-Properties Investigation

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The bistability of Spin Crossover (SCO) materials, caused by the switching of the central metal ion between high- and low-spin states (HS and LS), confers them great potential for technological applications in numerous fields, namely sensors, spintronics, memory and data storage devices. Switching can be triggered by external stimuli, such as temperature, light, pressure or guest inclusion. [1] Additionally, SCO can propagate from the central metal ion to all other physical scales, resulting in alterations of bond lengths, crystal volume, color etc. This cooperativity is even enhanced by the incorporation of SCO metal centers in metal-organic framework (MOF) scaffolds, [2] providing highly organized meso- or microporous channels and increased stability. [3]

In view of the utilization of these smart materials in functional sensing devices, we focus our attention on **1**, the $\text{Fe}_2(\text{H}_{0.67}\text{bdt})_4$ (bdt^{2-} = 1,4-benzenedithioborate) SCO-MOF, studying its structure-properties relationship in different conditions. Indeed, **1** is known for the water release induced spin switching, accompanied by a crystal color change from orange to blue and a 15 % volume decrease. [4] We study the effects of laser irradiation at room temperature on water desorption from the SCO-MOF, as well as its comparison with the thermal treatment, and the structural evolution by multiscale characterization techniques, including single-crystal X-ray diffraction (SC-XRD), Raman and Vis-NIR spectroscopy. Additionally, we investigate the electrical conductivity of **1** single crystals as a function of the metal spin state, when the transition from HS to LS is induced by thermal treatment or laser irradiation or viceversa by crystal rehydration. [5] All in all, the presented work paves the way towards the utilization of these class of materials in high-performance electrical devices.

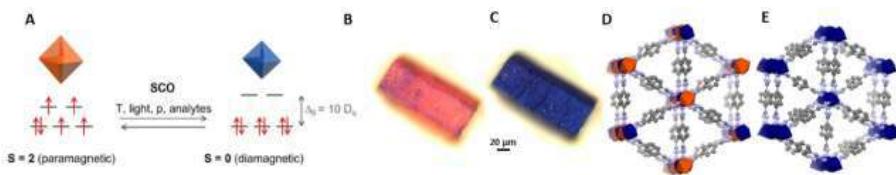


FIGURE 1. (A) Representation of the two spin states of an ion with d^6 configuration undergoing SCO between a (HS) paramagnetic and (LS) diamagnetic states. Optical image of a single crystal of **1** (B) in the as-synthesized state and (C) after laser irradiation. 3-dimensional perspective of **1** (D) in the as-synthesized state and (E) after laser irradiation. HS Fe(II) is represented in orange, LS Fe(II) in dark blue, N in light blue and C in grey.

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Plasmonic nanoparticle-mediated photothermia: nanothermometric temperatures and cellular-level thermal effects

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Hyperthermia involves raising body temperature above the normal physiological range to induce cancer cell death within tumor tissue. Nanotechnology and the development of nanomaterials have led to nanoparticle-mediated thermo-therapeutic strategies, enabling highly localized hyperthermia treatment with reduced side effects on healthy tissues [1]. Remarkably, these therapeutic effects can occur without a macroscopic temperature increase [2]. Thus, precise temperature monitoring is essential to assess thermal dose and potential side effects, highlighting the importance of nanothermometry in developing new techniques capable of probing and controlling temperature at the nanometer scale [3,4]. Additionally, correlating local temperature increases with the extent of cellular damage is crucial to obtain effective treatments while avoiding damage to healthy tissues. In this study, gold-based plasmonic nanoparticles were used as photothermal agents, internalized in a 3D glioblastoma tumor model to provide a more realistic heated tumor environment. Local temperature was measured using X-ray absorption spectroscopy (XAS) at the Au L₃-edge (11919 eV), demonstrating, for the first time, the versatility of this label-free, direct, and universal nanothermometry methodology in complex biological environments [5]. Cellular damage was analyzed using confocal microscopy and colorimetric assays, showing how photothermal therapy influence overall cell-cell interactions, cellular structure, and integrity at the cellular scale.

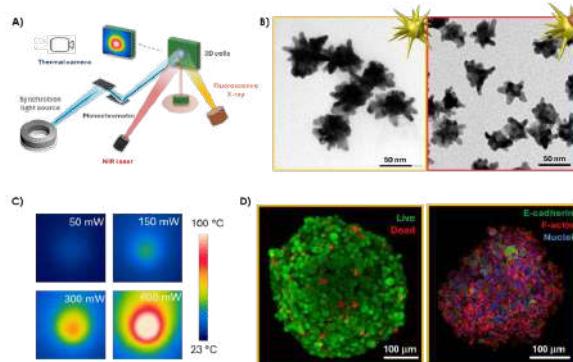


Figure 1. A) Experimental set-up of the XAS nanothermometry study. B) TEM images of the AUNs and Janus nanoparticles. C) Thermal images captured by the IR-thermographic camera. D) Confocal images of the 3D tumoral spheroids.

Notes and References

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Molecular Bilayer Nanographenes: the Search for Enantioselectivity

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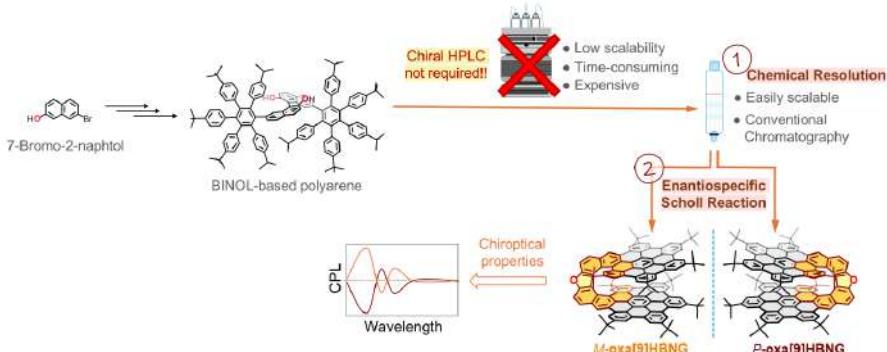
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Chirality is the geometrical property of structures that are not superimposable with their mirror images (enantiomers). Throughout the evolution of the different and varied areas of chemistry, controlling chirality has been both, highly challenging and useful. Its significance lies in the unique properties that chiral molecules exhibit. In the realm of material sciences, chiroptical properties, such as circularly polarized luminescence, are of particular interest. However, the selective synthesis of enantiomerically pure compounds remains a formidable challenge.

This work¹ focuses on the organic synthesis of nanometer-sized graphene fragments, known as molecular nanographenes, with highlighting chiroptical properties.² The synthetic path starts with 7-bromo-2-naphthol, a commercially available starting material. The sequence of oxidative coupling, followed by a double Sonogashira coupling and a [4+2] cycloaddition, leads to a BINOL-based polyarene. The central BINOL moiety induces axial chirality and provides two reactive functional groups. To achieve enantiomeric purity, we employ a classical yet powerful technique: chemical resolution. By introducing a chiral auxiliary, camphorsulfonyl chloride, the enantiomeric mixture is transformed into diastereomers. These diastereomers, possessing distinct physical and chemical properties, can be readily separated using conventional chromatographic techniques. Subsequent hydrolysis removes the chiral auxiliary, affording the pure enantiomers of the polyarene.

Finally, a Scholl reaction is performed on each enantiomer. The Scholl cyclodehydrogenation provides for the formation of multiple carbon-carbon bonds in the presence of oxidants and Brønsted acids. In this case, the Scholl reaction simultaneously leads to twelve covalent carbon-carbon bonds and an enantiospecific cyclodehydration of the central BINOL core, resulting in a pair of enantiomerically pure chiral bilayer nanographenes *M*-oxa[9]HBNG and *P*-oxa[9]HBNG.

Thus, this straightforward methodology is based on two key steps, a chemical resolution of enantiomers followed by an enantiospecific Scholl reaction. This methodology is expected to pave the way for new easily scalable and chemically affordable approaches to enantiopure chiral nanographenes, avoiding the time-consuming and expensive chiral HPLC separation of enantiomers.



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Exploring bacterial-surface interactions with a fluorescent membrane tension probe

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Fundamental aspects of the physical interactions between bacteria and surfaces are poorly understood, in part due to the challenges associated with their real-time characterization in a biologically relevant environment. In this work we are focused on understanding variations in membrane tension of bacteria (Gram positive and Gram negative) upon contact with different types of surfaces. To that end, we use Flipper-TR®, a fluorescent probe that reports on membrane tension through variations in fluorescence lifetime, which in turn are the consequence of changes in the twist angle and polarization between two dithienothiophene moieties ^[1,2,3] (Figure 1A). By using FLIM (Fluorescence Lifetime Imaging Microscopy), an advanced microscopy technique that is especially suited for sensing applications due to its independence on probe concentration or autofluorescence rejection, we show that Flipper-TR® is sensitive enough to report the interaction between bacteria with different surfaces (i.e. CellTak or Polylysine, Figure 1B-C)). Moreover, we show that membrane tension varies across Z-planes, and that Flipper-TR® can discriminate between membranes of different bacterial strains. Overall, this membrane tension probe is a useful tool to understand the complex interaction between bacteria and materials.

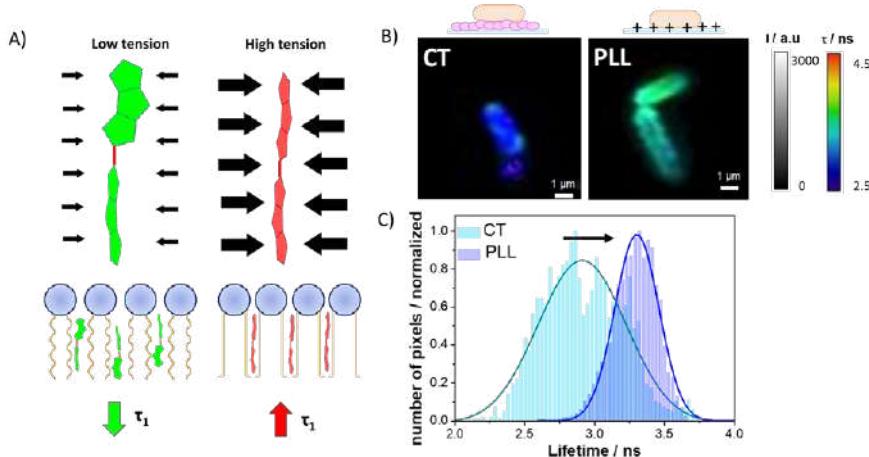


Figure 1. A) Conformation variations of Flipper-TR® according to differences in membrane tension. B) FLIM Images of *E. coli* BW25113 with Flipper-TR® on CellTak (CT) and polylysine (PLL). C) Fluorescence lifetime distributions of Flipper-TR® on *E. coli* BW25113 on CT and PLL.

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Cavity optomechanics in MoS₂ micro-drum resonators

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The field of cavity optomechanics explores the interaction between electromagnetic radiation and nanomechanical motion. Optomechanical devices are commonly used for the optical detection of displacements in the nanometric range, small masses or forces [1], and also could serve as coherent light-matter interfaces, for applications in quantum information processing [2].

In this work we study the optomechanical properties of MoS₂ micro-drum resonators. Radiation pressure and thermal effects of incoming laser light, can result in the coupling of optical cavity modes and mechanical drum modes, forcing the membrane to oscillate. The readout of the membrane response is performed via tracking the changes in the system's reflectivity.

By applying RF electric fields between the drumhead and the substrate in the range of (1,100) MHz, we can force electromechanical oscillations in the suspended region, to study the mechanical properties and the resonant modes of the membrane.

When the electrical driving and the optomechanical mode frequencies are close enough we observe and anticrossing behaviour characteristic of strongly coupled systems.

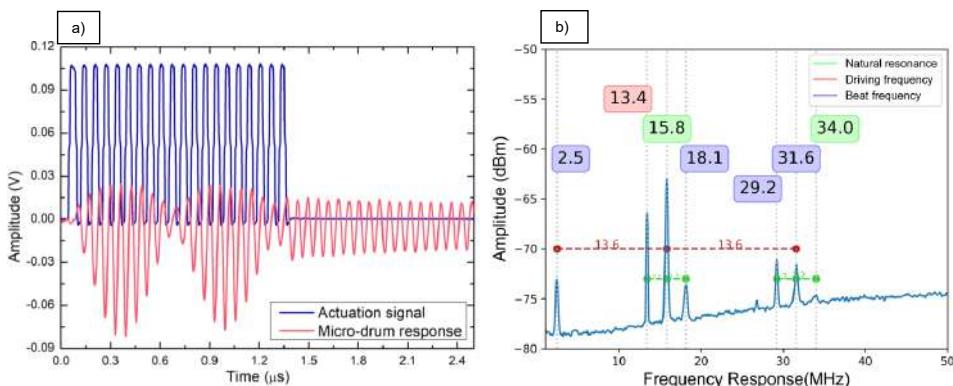


Figure 1: a) Driven and free response of the resonator under a burst with a frequency of 15 MHz. This graph shows the interaction between two oscillators through the beats in the signal response. b) Spectrum analyzer response of an electrically forced resonator (driving frequency) and the lower and upper sidebands

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Super-resolution microscopy reveals how viral infection reshapes host genome structure by sequestering RNAP II

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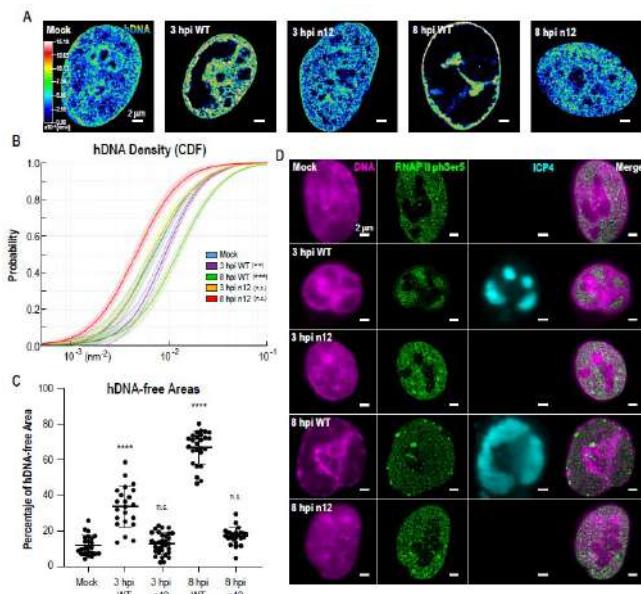
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Herpes simplex virus type 1 (HSV-1) remodels the host chromatin structure and induces a host-to-virus transcriptional switch during lytic infection. The mechanism of remodelling and the specific kind of folding produced on the host chromatin are still unknown. Using Super Resolution microscopy to identify the HSV-1 induced mechanism of chromatin compaction can offer us insights into the underlying mechanisms regulating the high order chromatin folding. We found that the the host chromatin massive condensation is caused by the hijacking of RNA polymerase II (RNAP II) to the viral replication compartment (VRC) by the immediate early viral protein ICP4. Furthermore, sequestered RNAP II was found to be highly associated to individual viral DNA (vDNA) clusters. This viral mechanism of host chromatin rewiring sheds light on the role of transcription in chromatin architecture.

FIGURE



A. STORM density rendering images of hDNA in mock or HSV-1 WT and HSV-1 n12 infected A549 cells. Scale bar: 2 μ m. Differences in DNA density follow the color scale bar. B. Cumulative distribution of the Voronoi polygon densities for hDNA distribution in mock, HSV-1 and HSV-1 n12 infected cells at 3 hpi and 8 hpi. Thick lines show the median and light colors, the interquartile range. ns, p > 0.05; ** p < 0.001, *** p < 0.001, Dunnett's multiple comparison test against mock. C. Percentage of hDNA-free area per nucleus of EDC-AF647 labeled hDNA in mock, HSV-1 WT and HSV-1 n12 infected cells at 3 hpi and 8 hpi. Mean and SD represented; ns, p > 0.05. **** p < 0.0001, Dunnett's multiple comparison test against mock. D. Conventional images of hDNA (magenta), conventional ICP4 (cyan), and STORM images of RNAP II phSer5 (green) in mock, HSV-1 infected cells and HSV-1 n12 infected cells at 3 and 8 hpi. Scale bar: 2 μ m.

Multifunctionalized Gold Nanoparticles for Biomedical Applications

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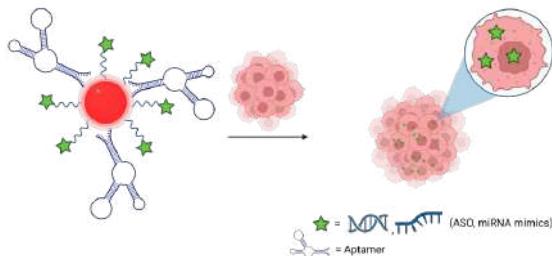
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Nanomedicines have emerged as innovative platforms for addressing complex diseases, where multimodal therapeutic approaches can potentially enhance treatment outcomes. Among these nanomedicines, nanoparticle-mediated nucleic acid delivery has been proposed as a key strategy to modulate gene expression through targeted gene silencing, RNA interference, and gene editing.[1] Concretely, gold nanoparticles (AuNPs) have emerged as particularly promising nanocarriers due to their tunable size, shape, and surface properties, which facilitate their functionalization with various biomolecules for efficient delivery.[2]

In this regard, our progress in this field will be presented. Particularly, functionalized nanoparticles have been successfully employed in different bioapplications: for gene silencing, by employing a smart linker for the delivery of modified antisense oligonucleotides in luciferase assays; and as immunostimulatory agents, acting as miRNA mimic delivery vector for the stimulation of immune cells towards melanoma cells. Moreover, we have demonstrated the targeted delivery of nucleic acids to muscle stem cells (MuSCs) using AuNPs functionalized with a cocktail of miRNA mimics and aptamers, showing excellent results in the recovery of muscle function in Duchenne Muscular Dystrophy mice model.[3]



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Acknowledgments

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Implementation of Spin-Orbit Torque biasing into manganite AMR sensors

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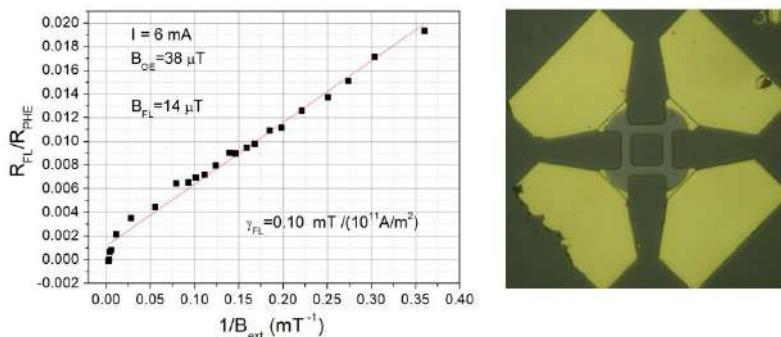
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$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) half metallic perovskite oxides are suitable materials for application as anisotropic magnetoresistance (AMR)-based low field magnetic field sensors [1], and in particular for implantable neural interface operating at human body temperature. These sensors, in fact, can combine reduced size, good sensitivities up to 0.3 mT , and low intrinsic noise in the low-frequency region with detectivity as low as $1.4 \text{ nT Hz}^{-1/2}$ [2]. These results are obtained in a Wheatstone bridge structure patterned on an LSMO single layer with well-defined uniaxial magnetic anisotropy realized exploiting vicinal surfaces [3]. To maximize the AMR signal, and hence the sensor's sensitivity, we can pattern the Wheatstone bridges with arms at 45° or at 0° and 90° with respect to the anisotropy axis. The maximum sensitivity is obtained in the region where magnetoresistance varies linearly with the field. Although the 45° configuration exhibits the linear region around zero field, the AMR signal is less prominent and presents a sensitivity one order of magnitude smaller than the case of 90° . The downside of the 90° configuration would then be that the linear region is at a finite magnetic field (i.e., at $H_0/2$ with H_0 being the anisotropy field), which is not practical for applications. To overcome this limitation, we can exploit the spin-orbit torque (SOT) effect to place the maximum sensitivity region at zero magnetic field in the 90° configuration. This is achieved by using the bias field (consisting of a combination of magnetic field-like (FL) and Oersted fields) created in a bilayer Pt/LSMO [4] that results from the generation of a spin current in the heavy metal due to the injection of charge current. Previous experiments on LSMO/Pt [5] indicate that this bilayer is adequate for the induction of SOT-related fields. In our study, we have estimated both the real and the imaginary parts of the spin-mixing conductance by the Ferromagnetic Resonance (FMR) technique [6] and calculated the FL efficiency (γ_{FL}) by using Harmonic Hall measurements [7], which has been shown to be $\gamma_{FL} = 0.1 \text{ mT} / (10^{11} \text{ A/m}^2)$, within the same order of magnitude than Pt/Pt [4]. This result suggests that SOT can induce a quantifiable shift in the sensor curve.



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Lipopeptides as tools to mimic life-like behaviour

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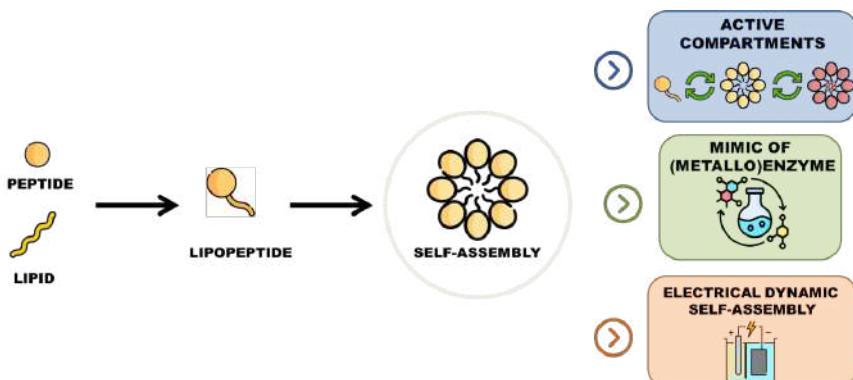
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Compartmentalization, replication, catalysis and evolution are fundamental aspects associated to living systems and played important roles in the emergence of functional (living) organisms.^[1a,b] Attempts to construct chemical systems resembling these features usually lack of a general perspective, focusing either on studying self-assembly compartments, thermodynamically stable replicators or chemically fuelled transient species without a particular functionality.^[2] Within this context, systems chemistry perspective offers a holistic framework to fully understand the plethora of interconnected reactions performing an advanced behaviour: dynamic self-assembling states, compartmentalized chemical networks or non-equilibrium regimen.^[3]

Lipopeptides are an exceptional example of amphiphilic molecules that self-assemble into functional structures offering an interesting applicability into a considerable number of fields.^[4a,b] However, identifying small lipopeptides and lipoamino acids with defined supramolecular behaviour, catalytic properties or biological activity is still a challenge.^[4c]

Herein, we present a set of examples where lipoamino acids and lipopeptides can be employed as potent tools for the rational design of new dynamic systems, allowing to mimic life-like properties. Firstly, an auto-catalytic procedure is employed to generate micellar structures formed by histidine-containing amphiphilic self-assembly. This supramolecular species performs an esterase-like activity, releasing new apolar components *in situ*, that increases the structural and functional complexity of the supramolecular system (i.e. vesicles).^[5] Secondly, a minimal oxidase copper-metallocenzyme mimic, based on the ATCUN (amino terminal Cu(II)- and Ni(II)-binding) sequence, has been designed to promote benzyl alcohol oxidation to its aldehyde under mild and prebiotic compatible conditions.^[6] Finally, we have implemented an electrochemical thiol-disulfide system as a robust model to achieve an out-of-equilibrium dynamic self-assembly triggered by an electrical current.



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Magnetometry Study of a Corrugated Magnetic Thin Film with Stable Antiparallel Domains

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Three-dimensional magnetic structures have direct applications in magnetic field sensing [1] or non-conventional computing [2]. New nanostructuration procedures allow the fabrication of well-defined nano-undulated ferromagnetic thin films. The structural modulation can form appealing 3D magnetic patterns during magnetization reversal as demonstrated in references [3] and [4]. However, the study of the magnetic reversal properties of such systems presents many challenges due to the low dimension of the magnetic features and their interplay with optical phenomena. We present an experimental study on the magnetooptical response of a 3D corrugated ferromagnetic thin film fabricated with a combination of laser interference lithography and DC sputtering techniques (Figure a) [4]. We perform angular Kerr measurements with different light colours such that the pattern features fall either in the subwavelength (red light) or in the diffraction regime (violet light). Violet Kerr measurements show new features on the magnetization reversal (Figure b) that we associate to the formation of 3D antiparallel magnetic domains. We confirm this magnetic distribution with micromagnetic simulations (Figure c) and magnetic force microscopy measurements at remanence. The occurrence of 3D magnetic states and the magnetooptical features associated with the diffraction regime characteristics in the studied system make it a promising material for magnetic sensing or computing applications.

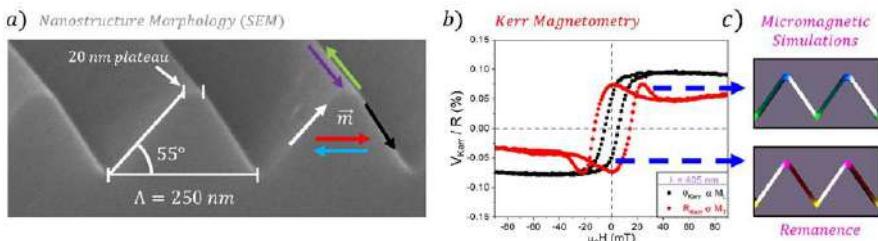


FIGURE. a) Nanostructure morphology of the corrugated sample obtained with lateral SEM, color scheme for micromagnetic simulations is shown in arrows, b) Violet Kerr effect measurements of Py-ST sample on hard axis, c) Micromagnetic simulations of relevant magnetic states during the magnetization reversal process.

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Innovative COF-Based Biosensor for Autism Spectrum Disorder (ASD) Biomarker Detection

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Currently, Autism Spectrum Disorder (ASD) has become a topic of interest for the general population, the scientific community as well as the healthcare system, since it affects more than 168 million people. This type of disorder is associated with language disorders, unusual motor behaviors, or social communication deficit. Early diagnosis of ASD is essential for developing treatments that improve the quality of life for those affected by enhancing their socialization and communication skills. However, current methodologies are slow, subjective, and do not allow early detection. Therefore, the search for biomarkers that enable the development of new methods for early, simple, quick, objective, and non-invasive detection is a priority research line. One of the most promising biomarkers for the early detection of ASD are miRNAs which are small, single-stranded, non-coding RNA molecules containing 21 to 23 nucleotides. The detection of these strands is carried out using classical techniques that present disadvantages, such as high cost or long analysis time. In this context, electrochemical DNA biosensors are presented as an alternative for miRNA detection that overcomes all the mentioned limitations. Nevertheless, there are some aspects that can be improved and need to be explored before practical devices can be developed. In this sense, the incorporation of nanomaterial such as Covalent Organic Frameworks (COFs) into these devices can be a good strategy to improve the analytical performance of these biosensors due to their exceptional characteristics (porosity, easiness of modulation, functionalization, etc.). Based on the above described, this study proposes the synthesis and characterization of a new COF for its use as electrochemical indicator in the development of a nanostructured DNA biosensor for the detection of miRNA-27a, an ASD biomarker. The design of biosensor (see Figure 1) is based on the combination of the new synthesized COFs and a bidimensional nanomaterial, Few-Layer Bismuthene (FLB).

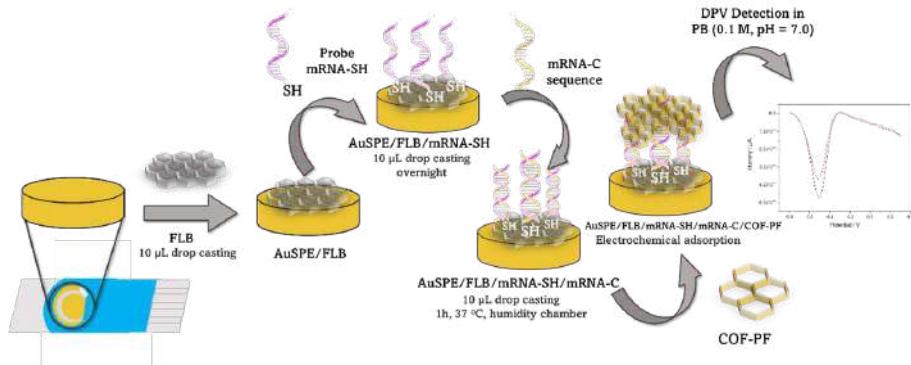


Figure 1. Scheme of the developed biosensor for ASD biomarkers detection

1,6-diazapyrene: A Model Nitrogen-doped Polyaromatic Hydrocarbon molecule for Spectroscopic and Quantum Mechanical Analysis

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Nitrogen-doped (N-doped) polycyclic aromatic hydrocarbons (PAHs) have found much interest in the past years to tune the electronic, optical and photophysical properties of PAHs, graphene, and carbon dots in (opto)electronic and (photo)catalytic applications.¹ The complexity of possible manifestations of N-PAHs demands the investigation of prototype systems, for instance by systematic structure variation, or computational screening of small model systems. For this, we envisioned 1,6-diazapyrene (DAP16) compound, and in-depth spectroscopic and (time-dependent) density functional theory, (TD-)DFT, analysis elucidated the optical excitations based on molecular orbital (MO) symmetry, energy and topology considerations (Figure 1), and unveiled the photophysical and -chemical deactivation kinetics after photoexcitation, revealing extreme changes against pyrene (Py) and the well-known 2,7-diazapyrene (DAP27).²

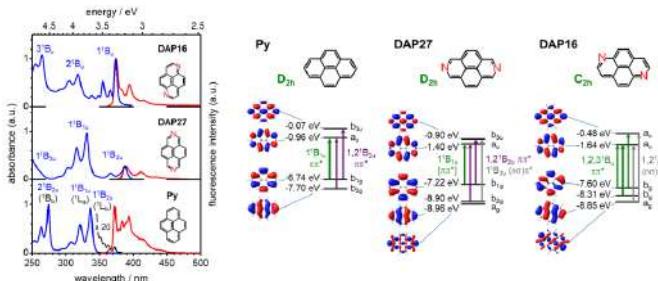


Figure 1. Comparison of spectroscopic and quantum mechanical data.

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Poster Communications



Poster Communications

Poster Communications

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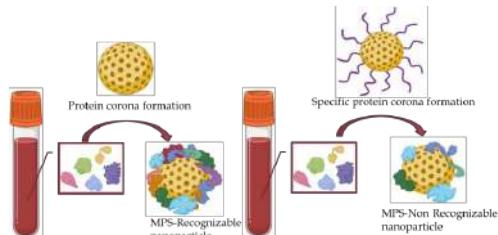
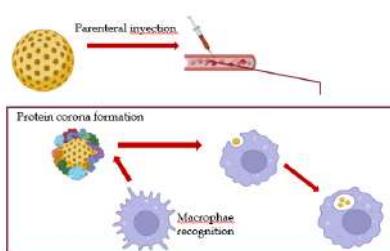
ANALYSIS OF THE VROMAN EFFECT IN MESOPOROUS SILICA NANOPARTICLES FUNCTIONALIZED WITH POLYETHYLENE GLYCOL

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When nanoparticles are administered systemically, proteins quickly accumulate on their surface, forming what is known as a protein corona. This new protein layer gives nanoparticles a distinct biological identity that can lead to their recognition by the immune system and their subsequent clearance from the bloodstream (Scheme 1). The formation of this corona is a dynamic process (Vroman effect), with the protein composition changing over time, which can influence immune recognition as the protein profile evolves. Polyethylene glycol (PEG) is commonly used to enhance the lifetime of nanoparticles in the bloodstream (Scheme 2), but the impact of the Vroman effect on this stealth coating has yet to be fully investigated.



Scheme 1 The mononuclear phagocyte system recognizes the protein corona that forms on the injected nanoparticles and phagocytizes them.¹

Scheme 2. Protein corona formed by the PEG inhibits the recognition of the nanoparticles from the MPS

In this study, we have employed mesoporous silica nanoparticles (MSNs) as model nanocarriers due to their favorable properties for drug delivery, including biocompatibility, high drug loading, and versatile surface functionalization. The MSNs were functionalized with PEG at two grafting densities and two molecular weights (2K and 5K). Protein coronas were formed by incubating the MSNs in human plasma for varying lengths of time, and the protein-coated particles were then tested with human macrophages to examine cellular uptake. This investigation provided insights into how PEG density and molecular weight influence protein corona formation and the resulting biological behavior of MSNs, offering useful guidance for designing improved nanocarriers.

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‡ Acknowledgments

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Re(I) vs Re(III) half-sandwich complexes. Synthesis, reactivity and biological studies.

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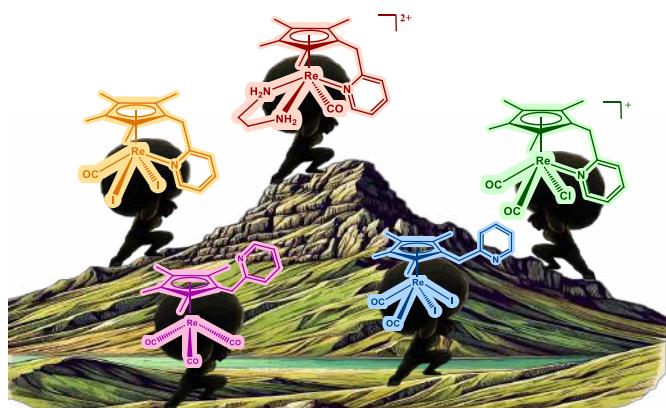
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Since the discovery of cisplatin, there has been an increasing interest in metal-based drugs for the treatment of cancer. Organometallic half-sandwich complexes of the platinum group metals are some of the complexes receiving attention as they have shown high potency against cancer cells.¹

Our group is focused on exploiting the organometallic half-sandwich structure to explore new chemical reactivities inside the human cells. For that, we work on complexes of formula: $[M(\eta^5\text{-Cp}^*/\eta^6\text{-areneR})XYZ]^{n+}$, which have only one labile position around the metal centre –only the metal-Z bond is susceptible to cleavage in aqueous solution– to allow for metal-based chemistry. Additionally, the Z ligand is anchored to the structure, they are *tether* complexes of formula $[M(\eta^5\text{:}^k\text{-Cp}^*\text{Z}/\eta^6\text{-areneZ})XY]^{n+}$, so that the cleavage of this ligand is reversible.^{2,3} Extensive SAR analysis on Ir(III), Rh(III), Os(II) and Ru(II) complexes has resulted in a >400 compounds library where we can control metal-Z reactivity by carefully choosing the metal and the ligands surrounding such a metal.

Rhenium half-sandwich chemistry is less studied and significantly different from Ir(III), Rh(III), Os(II) and Ru(II). In line with the same d^5 electronic configuration, we started our investigation on Re(I) half-sandwich complexes, $[Re^I(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{CO})_3]$. These complexes are inert towards substitution reactions at the tricarbonyl core, which precluded the coordination of several bidentate ligands and functionalities. To overcome this challenge, we focused on Re(III), which successfully allowed us to introduce different ligands, and to synthesise for the first time new families of four-legged piano-stool compounds with general formulae: $[Re^{III}(\eta^5\text{:}^k\text{-C}_5\text{Me}_4\text{R})X(\text{CO})_2]^+$, $[Re^{III}(\eta^5\text{-C}_5\text{Me}_4\text{R})X_2(\text{CO})]$, $[Re^{III}(\eta^5\text{:}^k\text{-C}_5\text{Me}_4\text{R})X_2(\text{CO})]$ and $[Re^{III}(\eta^5\text{:}^k\text{-C}_5\text{Me}_4\text{R})(\text{en})(\text{CO})]^{2+}$ ($X = \text{Cl}, \text{I}$).

Preliminary studies on the reactivity in DMSO and on the aqueous speciation of the new compounds have shown that Re(III) is more reactive toward substitution reactions than Re(I). Moreover, biological studies showed that Re(III) complexes are more cytotoxic than their Re(I) analogous, making Re(III) promising candidates for further studies.



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Exploring New Frontiers in Intracellular Chemistry with Half-Sandwich Organometallic Complexes: A Synthetic Overview on Cobalt(III) Derivatives

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Intracellular chemistry promoted by half-sandwich organometallic complexes of Ru(II), Os(II), Rh(III) and Ir(III) is a promising concept to modulate biological processes at molecular level, with impactful applications in medicine. The exciting results reported for precious metal complexes in the last decades¹ set the bases to expand the scope to other metal derivatives to enrich the palette of organometallic intracellular chemistry.

Cobalt is an essential d-block element present in many cofactors and redox enzymes. Some synthetic cobalt compounds have shown to combine interesting chemical properties and high versatility in biomedical applications.² Noteworthy, when compared to Rh(III) and Ir(III) analogues, half-sandwich organometallic Co(III) complexes display different thermodynamic and kinetic stability, higher electronegativity, harder character and a richer redox chemistry, involving several oxidation states (0,I,II,III and IV) accessible either via one- or two-electron processes. Whereas Co(III) complexes could be conceived as cheaper and more biocompatible alternative to Rh and Ir, in some cases they demonstrated unique reactivity patterns which allowed synthetic transformations not feasible with its noble congeners.³ On these bases the present project aims to explore the intracellular reactivity of newly synthesized Co(III) half-sandwich complexes (Figure 1) to unlock novel biologically-relevant chemical pathways with potential applications in biochemistry and medicine.

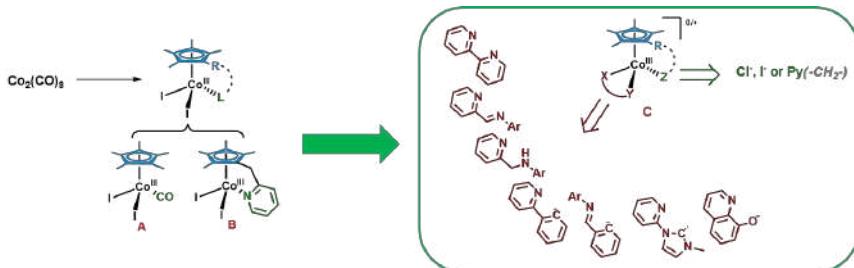


Figure 1

The first step of the project involves a comprehensive design of the complexes with the variation of the coordination environment to tune the delicate *reactivity-stability balance* in the biological environment. The general structure $[\text{Co}(\eta^5\text{C}_5\text{Me}_4\text{R})(\text{X},\text{Y})(\text{Z})]$ (C in Figure 1) is a highly versatile scaffold to develop tuneable compounds. Suitable cobalt precursors (A and B in Figure 1) can be obtained from commercially available $\text{Co}_2(\text{CO})_8$.

We have introduced two different functionalized cyclopentadienyl ligands, 1,2,3,4,5-pentamethylcyclopentadienyl (C_5Me_5) and 2-((2,3,4,5-tetramethylcyclopentadienyl)methyl)pyridine ($\text{C}_5\text{Me}_4\text{CH}_2\text{Py}$), with a tethered pyridine that binds to the metal centre, extensively studied by us in Rh(III) and Ir(III) complexes.⁴ Different X, Y- chelating ligands can be coordinated to the metal centre to diversify the stereo-electronic properties of the compounds. Neutral *N,N'*- and anionic *N,O*-ligands have been used to access cationic and neutral species, respectively. Cyclometallated *N,C*-ligands can be obtained through a base-assisted C-H deprotonation and metalation (CMD) reaction with suitable substrates. The remaining coordination Z position, which can be cleaved in biological conditions, can be an anionic ligand (chlorido or iodido) or can be occupied by the pyridine pendant from the Cp^* (tether ligand), affording modulation of the lability of this position in the aquation reaction.

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Reversible pH-responsive behaviour of ruthenium and osmium half-sandwich complexes bearing novel tethered-arenes

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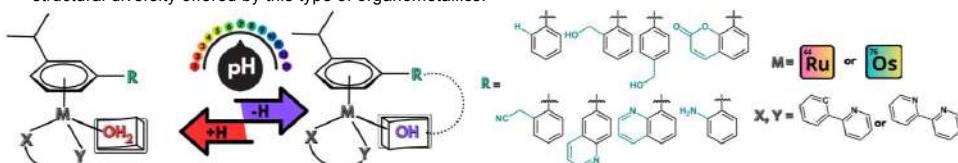
Ruthenium and osmium half-sandwich complexes have demonstrated to be excellent candidates for chemotherapy, with potent antiproliferative activity and selectivity against a variety of cancer cells both *in vivo* and *in vitro*,¹ in some cases equivalent and even more active than cisplatin. These complexes are also structurally attractive, since the modification of the components of the piano-stool geometry allows to modulate their chemical reactivity inside the cancer cells.² An important variable to consider in this kind of reactivity is the pH and its variation within the tumour microenvironment and within the cell, as a consequence of the Warburg effect.³ Depending on their structure, the chemical speciation of ruthenium and osmium half-sandwich complexes in aqueous media can be affected by pH, so they can act as pH-responsive switchable compounds.^{4, 5} A meticulous study of this behaviour can provide very valuable information about their possible chemical reactivity inside the cells, and thus serve as a guide for the rationale design of more efficient drugs.

Our aim is to design potent anticancer agents based on Ru(II) and Os(II) pro-drugs, varying the different parts of the piano-stool structure, especially the η^6 -arene –the less studied part in literature for this kind of complexes– to incorporate it as a hemilabile ligand that can lead to the formation of a tethered complex. In this tether complex, the η^6 -bound ring is strongly anchored to the metal, while the σ -bond between the pendant functionalisation and the metal centre can be reversibly cleaved, in response to certain stimuli such as pH changes. We also aim to comprehensively study how the complexes behave in aqueous solution, regarding pH-dependent speciation.

We developed a novel methodology to facilitate the derivatisation of the arene building block, which allowed us to synthesise new half-sandwich Ru(II) and Os(II) complexes bearing a number of attractive functional groups, some of them never seen before in osmium or ruthenium complexes (e.g. coumarin), and those that allow a tether-ring formation such as aniline and quinoline.⁶ The pH-responsive behaviour of this new complexes was mainly studied following their speciation by ¹H-NMR, plotting a titration curve (chemical shift vs pH), which allows to obtain the pK_a value of the protonatable functional group in the molecule, primary the aqua ligand.

Our results agree with previous work as we found that different arenes influence differently the speciation of our complexes in water. The arene also affects the pK_a values of the aqua adducts notably. Specifically, we found that alcohol-, coumarin-, and quinolone-arene complexes of formula [Ru/Os(η^6 -arene)bipy(OH₂)]⁺ have a more acidic pK_a (3.20–5.85). Interestingly, and also depending on the arene, the aqua ligand can lead to the closure of the tether-ring via intramolecular re-arrangement, as seen for example in complexes bearing the alcohol group, which aligns with earlier findings from our group.⁵

Our findings highlight the strong influence that the η^6 -arene of Ru(II) and Os(II) half-sandwich complexes in aqueous solution can have in their pH-responsive behaviour. Likewise, our novel synthetic methodology facilitates the rationale design of unique Ru(II) and Os(II) half-sandwich complexes, helping to take full advantage of the structural diversity offered by this type of organometallics.



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Nucleic acid functionalization of gold nanoparticles in a flow reactor

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Gold nanoparticles (AuNPs) have gained extensive attention in diverse scientific fields due to their unique optical, electronic, and catalytic properties¹. Their applications span from medical imaging, drug delivery, and photothermal therapy to biosensing and catalysis. However, there is a need for robust and sustainable manufacturing platforms for the delivery of high-quality, uniform-shaped, and monodisperse-functionalized AuNPs. In this sense, there have been several attempts to translate batch-made AuNPs towards continuous flow processing². Flow reactors display rapid heat and mass transfer, which minimizes particle size distribution while at the same time offering a tunable design³. Nevertheless, studies showcasing the in-line modification of AuNPs are scarce, and the use of nucleic acids is still missing⁴.

In this work, we have assessed the continuous synthesis and functionalization of AuNPs with molecules such as nucleic acids and polymers, and tested them for nanomedical applications such as biosensors and cancer cell treatment (Fig. 1).

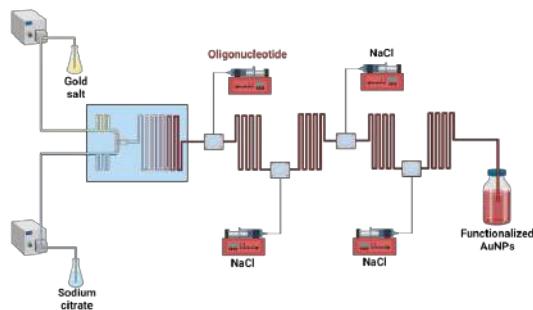


Fig 1. Flow reactor for the continuous synthesis and modification of AuNPs.

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Electrochemical DNA biosensor based on MoS₂-DNA tetrahedral bioconjugate for clinical applications

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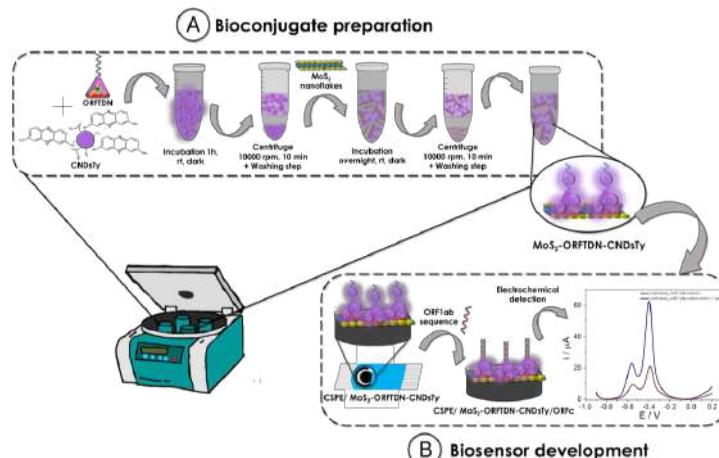
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In this work, we propose the development of an electrochemical DNA biosensor based on the preparation of a bioconjugate with the synergistic properties of molybdenum disulphide (MoS₂), tetrahedral DNA nanostructures (TDN) and thionine-modified carbon nanodots (CNDsTy) for virus detection. The MoS₂ nanolayers act as anchoring points for the TDNs, which carry the capture probe for the virus detection by its genetic code. To carry out the electrochemical detection of the hybridization event between the probe sequence and the analyte (virus sequence), TDNs are labelled with thionine-modified carbon nanodots that act as electrochemical indicators as they are able to interact directly with DNA. These CNDsTy present different affinity for the single-stranded DNA (ssDNA) or the double-stranded DNA (dsDNA), allowing the detection of the hybridization event. As proof of concept and due to the importance of developing new alternative detection methods, it has been tested for the detection of the specific SARS-CoV-2 ORF1ab virus sequence. The developed biosensor presents a detection limit of 5.00 fM and a linear range from 5.00 fM to 1.00 nM. In addition, this platform is not only able to detect infected patients in human nasopharyngeal samples, it also can distinguish between different viral loads.



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Optimization of Oligonucleotide Encapsulation into BSA Nanoparticles

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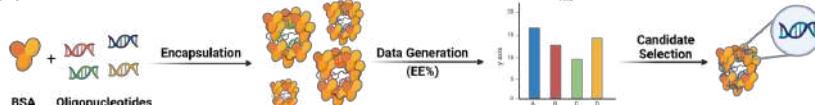
Nucleic acid-based therapies are highly effective in various diseases, including cancers. The molecules involved can be based on small interfering RNAs (siRNAs), antisense oligonucleotides (ASOs), messenger RNAs (mRNAs), or DNA plasmids (pDNA), among others¹⁻². However, these therapeutic approaches require vehicles (e.g., nanoparticles) due to poor stability, selectivity, and internalization of nucleic acids. Moreover, for the optimum design of these therapies, it is essential to use specific algorithms that facilitate the selection of the appropriate sequence depending on the target region¹⁻³.

In nanoparticle-based systems, one of the most relevant parameters is the encapsulation efficiency, since the efficiency of the system is highly dependent on this parameter. In this regard, to optimize this process, different parameters (e.g., amount of nanoparticle components, amount of nucleic acid, incubation time, etc.) are tested until the desired formulation is obtained⁴⁻⁶. Recently, García-Martín et al. described that the encapsulation of endogenous nucleic acids in extracellular vesicles is sequence-dependent and that certain structural patterns (motifs) allow better encapsulation. Therefore, these results suggest that the introduction of oligonucleotides with specific motifs (sequence) into the cellular interior can promote their transport by the organism in endogenous extracellular vesicles⁷. Albumin-based structures have great potential in biomedical applications. In fact, therapeutic agents such as (Abraxane®) are based on this biomaterial⁸.

Based on this background, the collaboration between IMDEA Nanoscience and Altenea Biotech aims to develop artificial intelligence to elucidate the structural motifs responsible for the most efficient incorporation of nucleic acids into therapeutic nanoparticles.

In this first part of the project, we focus on how we can optimize the process of encapsulation of oligonucleotides in albumin nanoparticles (BSA). To do this, we use a reference oligonucleotide chain of fixed composition (PolyT) but variable length, to which we incorporate a set of oligonucleotides (motifs) of both variable composition (adenine (A), thymine (T), guanine (G) and cytosine (C) or A+G) and length (4-6 nt). The first results show that domains containing pyrimidine bases (A,G), enhance the encapsidation compared to pyrimidine bases (C,T). This may be because their chemical structures favor interaction with the hydrophobic pockets that compose part of the albumin structure. Further studies are required to optimize the oligonucleotide sequence selection for better encapsulation efficiency and, assess their biological activity.

Figure 1



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Empowering the immune system by targeted nanoparticle-based precision delivery of immunoregulatory microRNAs to lymphocytes

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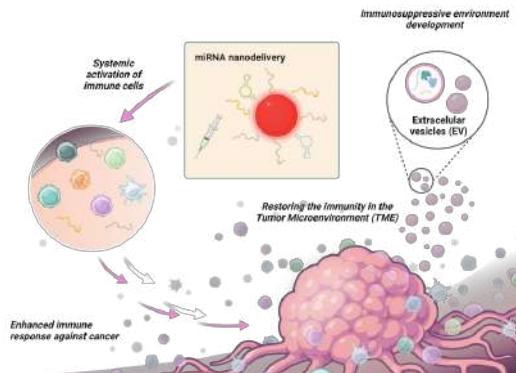
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The immune system is essential in protecting against cancer, but tumors, particularly melanoma, have evolved sophisticated mechanisms to evade immune detection. Melanoma, a highly metastatic skin cancer with high mortality rates (1), escapes immune surveillance establishing immunosuppressing microenvironment mainly by releasing small extracellular vesicles (sEVs) that impair T-cell function, leading to markers of exhaustion such as PD-1, TIM-3, and LAG-3. This immune escape challenges the efficacy of immunotherapies (ITs), which, despite their promise, face limitations like inconsistent patient responses, adverse immune effects, and tumor-induced immunosuppression, underscoring the need for more precise and effective approaches.

Recent studies suggest that microRNAs (miRNAs)—small RNA molecules that regulate gene expression—can influence immune responses in cancer (2). However, miRNA-based interventions are still limited in clinical application, particularly in the context of directly targeting immune cells and/or immune organs (3). Nanotechnology offers a potential solution, allowing for the development of targeted therapies (4). In this study, we explore nanoformulations designed to boost immunity in cases where immune function is compromised, such as cancer. Our approach involves creating and testing various carriers, including metallic nanoparticles, protein nanoparticles, and cellular carriers, to assess their potential for systemic immune targeting. In one application, we developed gold nanoparticles loaded with immunoregulatory miRNAs (miRNA-AuNPs) to counteract melanoma-induced immunosuppression. sEVs derived from highly metastatic melanoma cell lines (SKMEL103 and A375MA2) were found to suppress T cell activation and upregulate exhaustion markers (PD-1, TIM-3, and LAG3). miRNA-AuNPs, on the other hand, partially reversed this immune suppression by promoting the expression of T cell activation markers such as CD25 and CD69, demonstrating potential to restore immune function.

This interdisciplinary strategy brings together immunology and nanotechnology to address critical challenges in cancer treatment, aiming to advance nanotechnology-driven ITs as a viable approach to enhance immune responses against cancer.



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CRISPR-associated Plasmonic Colorimeter Method (Ca-PCM): a real-time RGB detection system for gold nanoparticles-based nucleic acid biosensors

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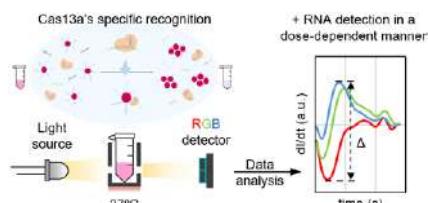
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Genetic testing constitutes a main tool for discriminating between species, characterizing tumors, or identifying pathogens. In this regard, plasmonic nanoparticles, such as gold nanoparticles (AuNPs), are considered powerful and versatile biosensors that offer high sensitivity, affordable costs and a user-friendly manipulation¹. However, the readout techniques typically used with these sensors hamper the possibility to implement quantitative detection since they do not provide temporal and kinetic information. To overcome these limitations, we have developed a new methodology named 'CRISPR-associated Plasmonic Colorimeter Method' (Ca-PCM). This technology combines the AuNPs' aggregation triggered by specific RNA target recognition by CRISPR LwaCas13a², and its real-time colorimetric Red-Green-Blue (RGB) analysis³. The system registers the AuNPs' plasmonic signatures through the aggregation process in real-time employing a RGB color sensor with blue, green and red sensitivities that covers the main changes that occur in the plasmonic spectrum. Then, the acquired signals are automatically analyzed by a designed algorithm that is able to distinguish between the positive or negative presence of the RNA target in the sample. Results show a correlation between the temporal spectral patterns of aggregation and the dose-dependent molecular detection of the RNA, enabling its 'quantitative-like' detection'. In addition, the combination of Ca-PCM with previous isothermal amplification reactions allows the target detection at the fm level, being compatible with real clinical applications. As a matter of fact, the evaluation of the method's suitability for the detection of SARS-CoV-2 in clinical samples (with Ct values < 28) reveals a positive predictive value of 97% and a negative predictive value of 100%, highlighting its potential as an effective diagnostic tool. Through the combination of RGB analysis and continuous temporal measurements, this novel methodology increases the possibility of characterizing the behavior of AuNPs-based biosensor and achieving dose-dependent target detection. In addition, its simple design and affordable cost expand the usefulness of other plasmonic-based biosensors and their applicability in low-resources clinical environments.



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Regulating long non-coding RNAs for Pancreatic Cancer treatment

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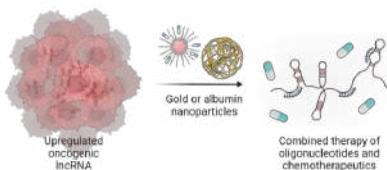
Pancreatic cancer (PC) is a very aggressive and metastatic cancer, with an increasing incidence and a low survival rate, due to its frequent late diagnosis and rapid progression. The usual treatment, if surgery is not possible, consists of radiotherapy and chemotherapy¹. However, their efficacy is very low, mainly due to the development of resistance by the tumor cells and the appearance of recurrent metastasis.

With the increasing importance of non-coding RNAs as crucial regulators of gene expression, new possibilities have emerged to explore therapeutic alternatives for the treatment of various pathologies, including cancer. Recently, a large number of long non-coding RNAs (lncRNAs) have been found to be involved in carcinogenesis, progression, and prognosis of cancer². Therefore, it is beneficial to have a tool focused on decreasing their oncogenic effects.

For this purpose, lncRNA FOXD3-AS1 was chosen as a therapeutic target due to its oncogenic role described in the literature³. First, FOXD3-AS1 expression levels were evaluated in the pancreatic cancer cell lines PANC-1 and BxPC-3, compared to the non-tumorigenic HPDE pancreatic cell line. Moreover, small interfering RNAs (siRNAs) and antisense oligonucleotides (ASOs) were designed⁴ to downregulate FOXD3-AS1 action. Their efficacy was tested by observing changes in FOXD3-AS1 expression and evaluating their effects on cell viability, in the pancreatic cancer cell lines PANC-1, BxPC-3 and MIA PaCa-2. In addition, cell cycle and cell death assays were performed by flow cytometry in the cell lines mentioned above, along with autophagy and oxidative stress studies.

Furthermore, we propose the use of gold and albumin-based nanoparticles as a strategy for the delivery of these oligonucleotides to the tumor to protect them from degradation, exploit the enhanced permeability and retention (EPR) effect to reach the tumor, and release their cargo in tumor-specific environments⁵. These nanoparticles were prepared to deliver the most efficient ASOs, and their hydrodynamic size, surface charge, and oligonucleotide loading were characterized. In addition, their delivery efficiency was evaluated by assessing the decrease in luciferase expression when loaded with an ASO against this gene.

The results are very promising, as it has been possible to design effective siRNAs and ASOs that decrease FOXD3-AS1 expression, leading to significant therapeutic effects. However, it is necessary to continue this research to improve this system and evaluate its performance in advanced models. Remarkably, the approach followed in this project can be applied to other target lncRNAs and other types of cancer.



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Single-molecule characterization of the auto-regulated human mitochondrial replicative helicase (Twinkle)

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The human mitochondrial replicative helicase, Twinkle, is a central component of the mitochondrial replisome and it is vital for replication and integrity of mitochondrial DNA (mtDNA). Therefore, investigating the real-time kinetics of Twinkle's activities and their regulation is crucial for understanding mtDNA replication. Here, we combine biochemical and single-molecule manipulation and visualization techniques to investigate the loading of Twinkle onto the DNA fork, its real-time DNA unwinding/rewinding kinetics, and the regulation of these processes by the amino- (N) and carboxyl- (C) terminal ends of the helicase and the mitochondrial SSB protein (mtSSB). We observed that upon self-loading, Twinkle oligomers rapidly diffuse along dsDNA. Diffusion enables the helicase to efficiently scan for the forked DNA, where it establishes specific interactions that stall diffusion. Our results showed that during DNA unwinding, the real-time kinetics of the helicase are downregulated by interactions of its N-terminal Zinc-binding domain (ZBD) with DNA and the control of the ATPase activity by the C-terminal tail. We found that binding of mtSSB to DNA likely outcompetes for the ZBD-DNA interactions, alleviating the down regulatory effects of this domain. Furthermore, we showed that ZBD-DNA interactions together with the ATP-bound state, control the real-time kinetics of DNA rewinding events found upon helicase stalling. Our findings portrait Twinkle as a strongly auto-regulated helicase, which would be relevant to control its mtDNA maintenance activities.

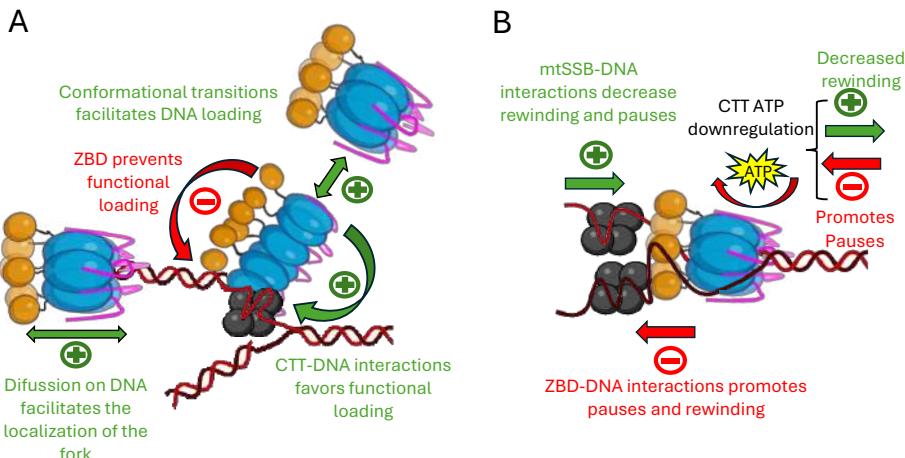


Figure 1. A) Diagram illustrating Twinkle loading onto a DNA fork already coated with mtSSB, showing how loading may occur either by cracking its oligomeric structure or by diffusion along the dsDNA. The "+" and "-" symbols indicate how the ZBD and CTT domains modulate the loading function positively or negatively. B) Diagram illustrating Twinkle's helicase activity, and how this activity is negatively regulated by ZBD-DNA interactions, which can be alleviated by mtSSB. The diagram highlights the dual role of CTT in downregulating ATPase activity, resulting in decreased rewinding and promoting pauses.

Development of a FRET-based sensor to monitor the activity of BACE1 in live cells

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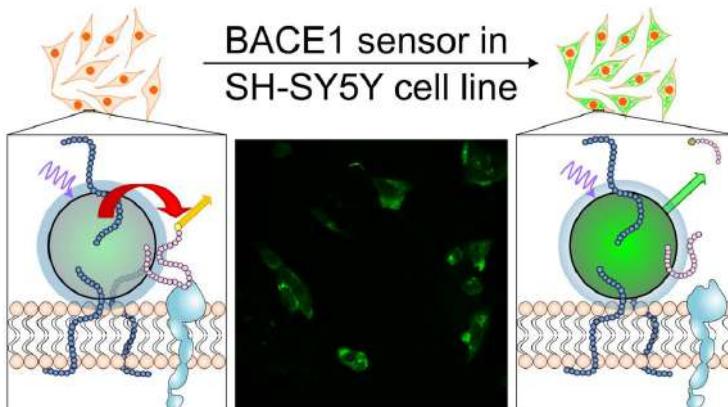
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Alzheimer's disease, the most common neurodegenerative disorder affecting 55 million people worldwide, is becoming more prevalent as the global population continues to age. However, it currently lacks an efficient cure and its etiology remains unknown, hampering the development of effective therapies. β -Secretase, the β -site amyloid precursor protein cleaving enzyme (BACE1), is the protease responsible for generating the β -amyloid peptide, a key factor in disease progression and a major therapeutic target. However, an understanding of its activity, modulation, and regulation remains challenging. This is in large part due to the complex nature of monitoring its activity. Beyond the common requirements for all biosensors (ease of preparation and use), BACE1 probes also demand both stability at acidic pH¹ and membrane localization². To meet these requirements, we developed a fluorescent quantum dot (QD) sensor that leverages modular self-assembly. QDs offer enhanced fluorescence brightness and photostability when compared to traditional fluorophores. Furthermore, its larger surface area allows for functionalization with peptide substrates and targeting elements to localize the sensor precisely, achieved through His-tag self-assembly.³ In vitro, the sensor demonstrated stability under acidic conditions, and using high-throughput plate reader assays, we determined BACE1 activity in-line with literature values and enabled the obtainment of the inhibitor constant of verubecestat, a small molecule inhibitor. The sensor was also applied to cellular assays in neuroblastoma cell line, demonstrating sensitivity to BACE1 activity and its modulation by inhibitor treatment.⁴



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CRISPR RNPs delivery by iron oxide magnetic nanoparticles

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CRISPR/Cas technology has revolutionized genome editing since it provides a versatile toolbox for knockout and knock-in generation, base-editing and transcriptional modulation¹. Although CRISPR/Cas systems hold great promise in medicine, delivery into target cells is still a matter of concern. Delivery of pre-assembled Cas endonuclease and guide RNA (gRNA) ribonucleoprotein (RNP) complex has emerged as a revolutionary strategy due to its efficacy and safety². Integrating nanotechnology as vehicles for RNPs can also enhance its feasibility in vivo. Several nanomaterials can be used, but magnetic nanoparticles (MNP) are particularly attractive because of their safety and tunability³.

For these reasons, the present work aims to design a nanodelivery strategy through the conjugation of Cas9 or Cas12a RNP with carboxymethyl dextran-coated iron oxide magnetic NP for the gene editing of different cell lines. To address this challenge, we characterized MNP-RNP complexes, obtaining an efficient binding by a combination of both electrostatic and covalent interactions with good stability. Afterwards, we explored the delivery and gene editing efficacy of MNP-Cas12a and MNP-Cas9 in HEK-uGFP and MEF-tdTomato fluorescence-based reporter cells, respectively. We observed that nanocomplexes can be taken up by mammalian cells, decreasing the number of GFP+ cells and increasing the number of Tomato+ cells. Altogether, these findings indicate that MNP are suitable vehicles for the intracellular delivery of Cas RNPs, which can display specific gene-knockout activity. Genetic disorders are the main objectives for CRISPR therapeutics, so then we wanted to exploit the potential of MNP-RNP to target and correct the genetic changes underlying such disorders. To this end, we designed specific gRNA to target endogenous genes in genetic human disease cell lines.

To sum up, in this study we developed a novel nanotherapeutic strategy for the delivery of Cas RNP into target cells, which exhibit efficient gene editing and is likely to be used as a genome editing tool for the knock-out of disease-causing mutations.

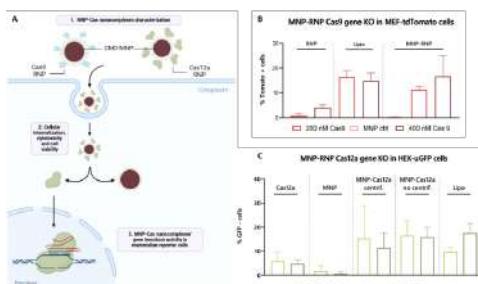


FIGURE. A. Schematic representation of MNP-RNP nanocomplexes conjugation, cellular internalization and gene editing mechanism. **B.** Flow cytometry of transfectected MEF-tdTomato cells. Knockout efficiency of MNP-Cas9 was remarkably higher at 400 nM than at 200 nM and this efficiency was comparable to that of lipofection. **C.** Flow cytometry of HEK-uGFP cells transfected with 400 nM of Cas12a using CMD-MNP nanoconjugates or Lipofectamine2000. MNP-Cas12a nanocomplexes were able to reach a gene editing efficiency similar to the commercially alternative Lipofectamine2000. Different times of incubation and centrifugation were tested.

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Biophysical study of aneuploidy in blood cancer cells

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We can find hematopoietic stem cells in the bone marrow that give rise to three different types of blood cells: red blood cells (transport of oxygen in the blood), white blood cells (defense) and platelets (coagulation). Genetic modifications in bone marrow precursor of white blood cells give rise to structural chromosomal alterations, such as translocations, and numerical alterations or aneuploidy. These alterations are able to transform the healthy cells into tumor cells, showing different biophysical properties and originating blood cancers. There are different types of blood cancers: **leukemia** is caused by the increased proliferation of bone marrow precursor cells, differentiating into lymphoid, if the lymphocytes are affected; or myeloid if, in addition to lymphocytes, the production of polymorphonuclear cells increases. On the other hand, **multiple myeloma** is due to an increase in plasma cells, or antibody producers, in the bone marrow. This research proposes the study of biophysical nuclear parameters applied to tumor cells with aneuploidy and compared to healthy cells, for their application in the early diagnosis of blood cancers.

For this prospective work, three cell lines with chromosomal numerical variations were used: U266 (hypodiploid, multiple myeloma), Jurkat (hyperdiploid, acute lymphoblastic leukemia) and healthy T lymphocytes (diploid). Time-lapse microscopy and computational analysis by multiple nuclear particles tracking were applied to study the morphology, microrheology and nuclear movement of cells. Our results revealed an inverse relationship between size and chromosome number in lymphocytes. At the same time, there were dynamic differences between healthy and tumor cells, observing limited chromatin movement and less malleability in hyperdiploid lymphocytes compared to healthy T lymphocytes. Therefore, aneuploidy gives rise to biophysical nuclear differences that are an effective tool in the diagnosis and classification of patients with blood cancers.

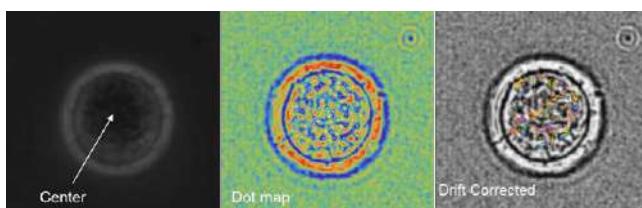


Figure 1. Analysis by multiple nuclear particles tracking. (Left) Healthy alive T Lymphocyte at the phase contrast microscope; (center) computational analysis by multiple nuclear particle showing the dot map of nuclear chromatin and (right) selection of every single trajectory of dots after drift correction.

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NIR-II Lanthanide-doped nanoparticles and click chemistry for heart inflammation imaging

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Lanthanide-doped nanoparticles (LnNPs) are characterized by a strong luminescence emission in the near-infrared, that can be exploited for the bioimaging of biological processes with a high resolution and sensitivity.[1] To take advantage of this, in this project we resorted to click chemistry to specifically target ICAM-1, an adhesion molecule that is overexpressed in inflammatory contexts and that is upregulated after an ischemic episode.[2] For this purpose, a specific antibody against ICAM-1 (Ab) and Neodium/Ytterbium (Nd3+/Yb3+) doped LnNPs were functionalized with the click groups trans-cyclooctene (TCO) and tetrazine (Tz) respectively, in order to selectively recognize the infarcted area through a specific bioorthogonal reaction of click chemistry. The experiments were carried out ex-vivo in a Langendorff heart perfusion system, where rat hearts were subjected to global ischemia for 45 min. Control hearts were maintained perfused with Krebs solution all over the experiment. After the ischemia, hearts were first infused with the anti-ICAM-1 Ab bond to TCO for 30 min and then with the LnNPs bond to Tz for 15 min. Subsequently, the explanted hearts were analyzed by infrared fluorescence imaging to calculate the ratio between the intensity of emission at 975 nm (specific emission of the Yb3+ present in the shell of the LnNPs)[3] and 940 nm (autofluorescence of myocardial tissue). Afterwards, the hearts were processed to further analyze the presence of ischemia by tetrazolium staining, the expression of ICAM-1 by immunohistochemistry, and the presence of apoptosis by TUNEL immunofluorescence. Our results confirm the presence of ischemia, ICAM-1 overexpression and apoptosis in ischemic hearts compared to healthy hearts. Moreover, the ratio 975/940 nm was significantly higher in ischemic hearts compared to controls ($p<0,05$). This result sheds light on the great potential that the combination of LnNPs and click chemistry has in the detection of ischemia in the myocardial tissue.

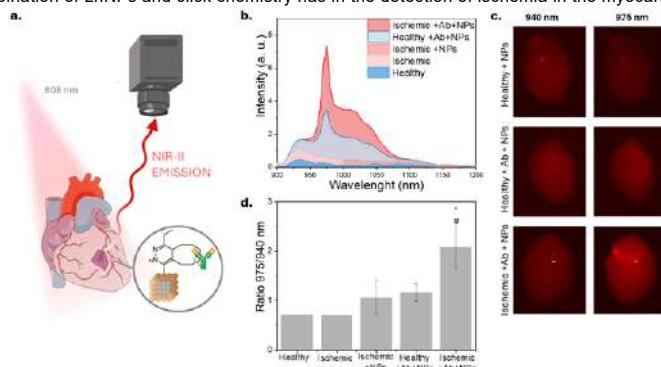


Figure. Graphical abstract (a); Hyperspectral fluorescent spectra (b) and images (c) of an ischemic heart infused with ICAM-1 antibody and Ln-doped nanoparticles, a healthy heart infused with ICAM-1 antibody and Ln-doped nanoparticles, an ischemic heart infused with Ln-doped nanoparticles, an ischemic heart, a healthy heart. Fluorescence intensity ratio (%) (d) between the wavelength 975 nm and 940 nm.

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Synthesis of magnetic nanoparticles with DMSA and their behavior in vitro

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Magnetic nanoparticles' (MNPs) ability to transform electromagnetic energy into heat offers enormous promise as a non-invasive therapeutic approach for biomedical applications. For tumor suppression, magnetic hyperthermia can be utilized to provide localized heating. The temperature at tumor areas can be raised significantly, lowering the viability of cancer cells (Liu et al., 2012). In addition, it is possible to combine magnetic iron oxides with other materials that bring other interesting properties (e. g. optical) in hybrid nanostructures.

This study aims to explore the effects of various MNPs and hybrid MNPs on cells. The thermal decomposition of metal precursors was used to prepare MNPs, Au-MNPs, and AuCu-MNPs with different morphologies (Figure 1). The nanostructures were then transferred to water by surface modification and characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA), UV-Vis spectroscopy. The magnetic heating abilities, under alternating magnetic fields, as well as their efficiency to act as contrast agents in MRI were also studied. The cytotoxicity and the generation of reactive oxidative species (ROS) at different concentration and incubation times were assessed.

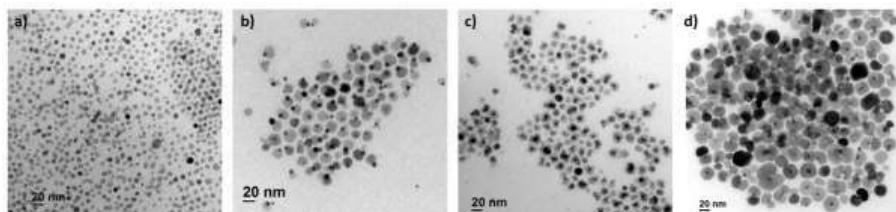


Figure 1. Different shapes and morphologies of iron oxide MNPs. **A)** Spherical shape Fe₃O₄ NPs. **B)** Spherical shape Fe₃O₄-Au hybrid MNPs. **C)** Flower-like Fe₃O₄-Au MNPs. **D)** Fe₃O₄-AuCu MNPs.

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Temperature impact on the real-time kinetics of the human mitochondrial DNA polymerase

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Mitochondria are eukaryotic organelles essential for energy generation. Mitochondria harbor their own DNA (mtDNA), which is replicated by the mitochondrial replisome (comprised of Polγ, Twinkle and SSBs) (1). mtDNA replication takes place inside the inner membrane of the mitochondria, a compartment that can reach temperatures of up to 50°C, some recent studies suggest (2). We aim to shed some light into the effects of increasing temperature on the real-time kinetics of the mitochondrial replisome operation. Here, we used optical tweezers with a temperature controller (3) to study at the single-molecule level the real-time kinetics of DNA replication activity of the DNA polymerase PolG, the effects temperature has on its pausing behavior and activation energy.

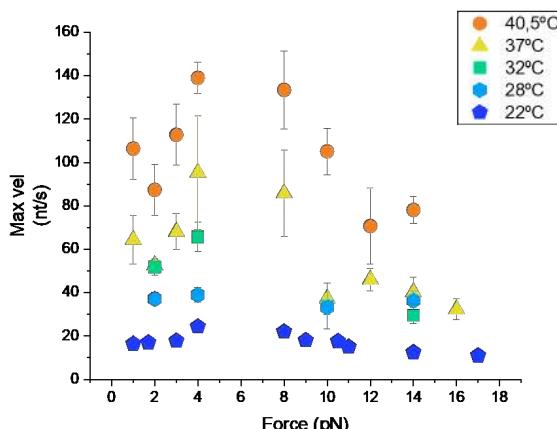


Figure 1. Higher temperatures increase the velocity of PolG. For each molecule held at a specific force, the highest polymerization speed is taken and averaged to give the points of the plot (each point with N:4-6). Different color curves indicate different temperatures.

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Poliploidy in hepatocytes: a study for early diagnosis of liver diseases

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The liver is a major metabolic organ which performs many essential biological functions such as digestion and processing of substances. Any pathology affecting this organ can alter the homeostasis of the whole organism. This metabolic and regulatory activity is controlled by the genetic structures of nuclear chromatin. The polyploidy present in hepatocytes and liver damage seem to be closely related, suggesting that these cells participate both in the detection of abnormalities in the organ and as a restorative mechanism of the organ. Therefore, analyzing their ploidy status would be especially useful to evaluate the evolution of different liver pathologies.

In this study, healthy adult mouse hepatocytes were used and they were extracted by perfusion (*in vivo*). In these cells, biophysical properties of the cell nucleus were assessed using time lapse video microscopy, and morphological properties, using fluorochrome labeling. The correlation between structure and nuclear activity was analysed and the nuclei of live mononucleated and binucleated cells were differentiated, as well as the increased activity of the nucleus considered master in binucleated cells. The study was completed with the analysis of the influence of interleukin-6 on the activation state of the hepatocyte according to its nuclear activity. Morphocytometric analysis made it possible to determine the interrelationship between nucleus, mitochondria, lysosomes, as well as the presence of reactive oxygen species during cell activity.

FIGURE

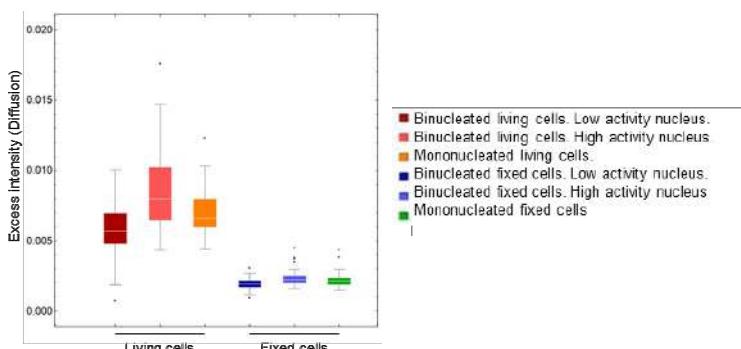


Figure1. BoxPlot to compare the activity of living and fixed cells, and also, the activity of nuclei of living cells with each other.

Single-molecule manipulation of genome integrity guardians

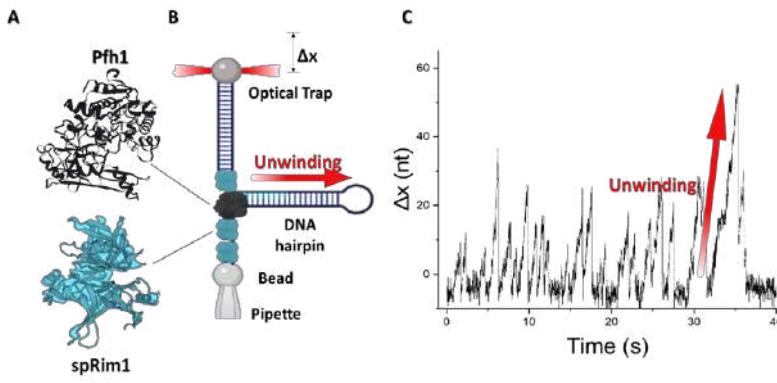
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DNA helicases of the Pif1 family are essential for maintenance of nuclear and mitochondrial genomes, acting as a guardian of its integrity. In coordination with other protein partners, Pif1 helicases work as molecular motors that unwind duplex nucleic acids and remodel nucleic acid-protein complexes driven by the energy from ATP hydrolysis. How these motor proteins open the DNA, how they couple chemical (ATP binding and hydrolysis) and mechanical (DNA unwinding) reactions, and how their behavior is modulated by protein-partners, such as single-stranded DNA binding (SSB) proteins, are questions under intense debate. To address these questions, we have developed an optical tweezers assay to follow in real-time and manipulate mechanically the DNA unwinding activity of individual Pif1 helicase molecules. Here, we describe the effect of fork stability and ATP concentration on the real-time DNA unwinding kinetics of the Pif1 helicase to unravel the mechano-chemical processes (energy conversion to work) that govern its operation. In addition, we show how binding of spRim1 SSB proteins to DNA modulates the real-time kinetics of the helicase.



Notes and

Fig. 1. **A.** Pfif1 helicase (grey) and spRim1 SSB (blue) structures. **B.** Schematic representation of the experimental set up with optical tweezers. A single DNA hairpin is tethered between two functionalized beads and held at constant force. One strand of the hairpin is connected to the bead in the optical trap (red cone) through a handle via digoxigenin-antibody connections. The other strand is attached to a bead on a micropipette by biotin-streptavidin linkages. At constant force, DNA unwinding by Pfif1 increases the end to end distance on the DNA molecule (Δx) which is followed in real-time with high spatial (1–10 nm) and temporal (500 Hz) resolutions. **C.** Characteristic DNA unwinding traces of Pfif1, showing that the helicase unwinds DNA through fast repetitive cycles of activity.

Effect of morphology and size of magnetic nanoparticles on cell viability.

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Superparamagnetic iron oxide nanoparticles (IONPs) have been widely studied for biomedical applications, as contrast agents in magnetic resonance imaging (MRI) and for magnetic hyperthermia treatments. In magnetic hyperthermia, IONPs release heat when they are subjected to an alternating magnetic field (AMF). IONPs heating abilities can be compared using the measured specific absorption rates (SAR) obtained from the experimental temperature vs. time variation under AMF [1]. The structural and colloidal properties of the particles (i.e. particle size, shape, aggregation state, interactions), the dispersion medium and the AC applied field (frequency and amplitude) determine the heating abilities of IONPs [2].

We have developed an environmentally benign synthesis method to prepare IONPs that allows fine tuning their composition, size, and morphology. The IONPs were coated with organic molecules to improve colloidal properties. Characterization was carried out by transmission electron microscopy (TEM) and X-ray diffraction analysis, and vibrating-sample magnetometry. Their suitability to act as contrast agents in magnetic resonance imaging was studied by time-domain nuclear magnetic resonance and calorimetric measurements under AMF were employed to determine their SAR values.

In this work magnetic nanoparticles with different sizes (16, 21, and 28 nm) and shapes (spherical and cubic) were tested at two different conditions of field and frequency. Finally, the cytotoxicity in two different linear cells, MCF-7 (breast cancer) and PANC-1 (pancreatic cancer), has been studied.

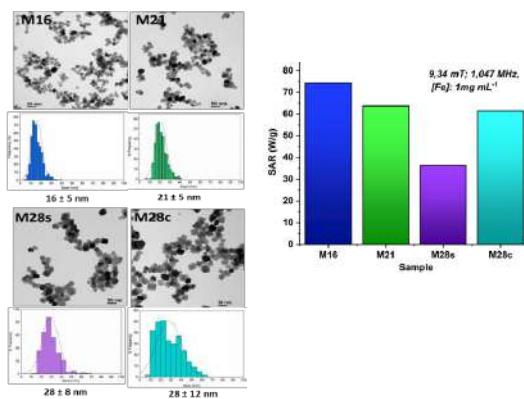


Figure 1. Selected TEM micrographs (left) and SAR values (right) of the IONPs studied in this work.

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Optimization of Ni electrodeposition parameters for the fabrication of neural interfaces

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Neurological disorders are on the rise in developed countries, driven by changing lifestyles and increased life expectancy. Neural interfaces that can record or stimulate neural activity have become vital tools for diagnosing and treating these conditions. However, current interfaces face several challenges, including being larger than ideal, which can result in non-specific stimulation and potential side effects. They can also lose effectiveness due to the body's foreign-body response, leading to encapsulation by a glial scar and the need for replacement. As a result, advancements in neural implants that interact with neurons in a less invasive manner have become a crucial area of research in nanobiomaterials (1,2,3).

In this context, our research aims to improve the effectiveness of neural interfaces intended for implantation by incorporating nanostructures onto the surfaces of neural electrodes. These nanostructure has the potential to enhance electrical properties by increasing the effective area, and reducing the electrode impedance (4). Consequently, smaller electrodes can be produced for more precise stimulation and reduced unwanted side effects. Additionally, the nanostructures promote closer contact between neurons and electrodes.

We propose implants with a flexible polymeric base and thin nanostructured metallic active pads. To achieve this goal, our strategy starts by depositing a thin metallic layer over a nanoporous template, followed by nanowire (NW) growth over its surface by filling the template nanoporous using electrochemical deposition. A polymeric layer is then deposited in the back of the metallic base before dissolving the template at its top. Using Ni as initial base material, the parameters of electrodeposition, like pulsed or continuous growth or the electrodeposition time, as well as the nature of the polymeric layer (Ormocomp, polyimide ...), are being optimized.

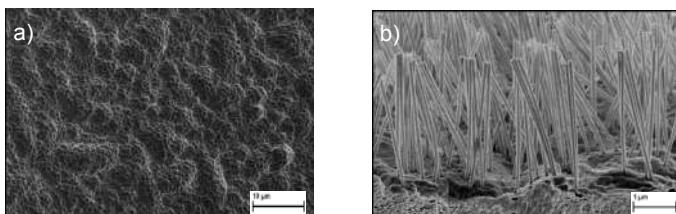


Fig. 1, SEM images of a) back side of a Ni base on a commercial polycarbonate nanoporous template b) representative Ni-NWs nanostructured electrode in lateral-view

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Benzothiazole-based Proteolysis Targeting Chimeras of Casein kinase 1 (CK1) for targeting Circadian Clock Dysfunction in Alzheimer's disease (AD)

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Alzheimer's disease (AD) is a complex neurodegenerative disease characterized by the accumulation of misfolded proteins, synaptic dysfunction, and progressive cognitive decline often accompanied by significant disruptions in circadian rhythms and sleep-wake cycles. Emerging evidence suggests a significant involvement of circadian rhythm dysregulation in the pathogenesis of AD.¹ Protein kinases such as Casein Kinase 1 (CK1) play a crucial role in circadian clock regulation,² and targeting these dysregulated kinases may provide a new therapeutic approach for AD. PROteolysis TArgeting Chimeras (PROTACs) are heterobifunctional molecules that induce the ubiquitin-mediated degradation of specific proteins of interest (POIs), offering a unique approach to regulating protein levels rather than their activity.³

For that purpose, a small library of CK1-targeting PROTACs was designed and synthesized based on benzothiazole derivatives originally developed for Amyotrophic Lateral Sclerosis (ALS), with promising potency, proven BBB permeability and explored SAR.⁴ Within this series, a combination of three different positions on POI ligand, two on cereblon recruiter, and two different linker lengths will be examined to determine optimal geometry for formation of effective ternary complexes. Currently, synthesis of the first series is complete, testing for in vitro potency and initial pharmacological and ADMET evaluation is in progress, as well as viability, degradation, and neuroprotection studies to deliver proof of concept of these compounds.

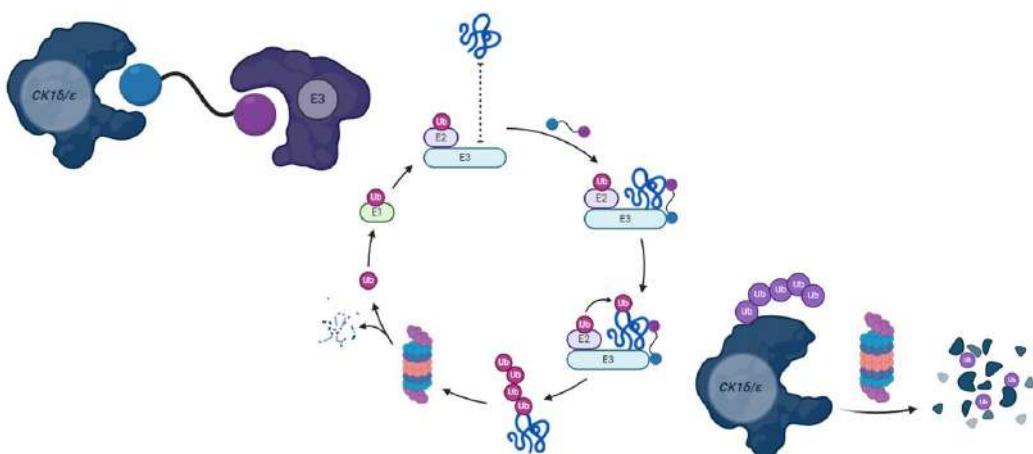


FIGURE 1 PROTACs mode of action

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Optimizing LNP-mediated CRISPR/Cas13b Cell Delivery for Enhanced Gemcitabine Sensitivity in Pancreatic Cancer Cells

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Pancreatic ductal adenocarcinoma (PDAC) is among the most aggressive cancers and is associated with a particularly poor prognosis. For patients with metastatic PDAC, gemcitabine, either alone or in combination with other agents, is the current standard treatment. Nevertheless, PDAC cells frequently develop resistance mechanisms that limit gemcitabine's efficacy¹. An alternative therapeutic strategy involves the use of CRISPR-based systems. Specifically, approaches using Cas13b ribonucleoproteins (RNPs), which rely on Cas13b's cleavage activity to target and degrade specific single-stranded RNAs, could allow for the selective silencing of anti-apoptotic genes, thereby enhancing PDAC sensitivity to existing antitumor therapies. In this context, survivin, an anti-apoptotic protein encoded by the BIRC5 gene, has been identified as a key factor contributing to chemoresistance in pancreatic cancer^{2,3}. Studies have shown that downregulation of survivin reduces pancreatic cancer cells' resistance to gemcitabine. However, challenges remain with this approach, particularly in terms of efficient delivery into cells. Lipid nanoparticles (LNPs) have shown promise as carriers for delivering CRISPR/Cas systems in various forms, including DNA, RNA, and recently as RNP^{4,5}. The objective of this study is to assess whether transfecting Cas13b RNPs targeting BIRC5 in pancreatic cancer cells can knock-down survivin expression and enhance sensitivity to gemcitabine as an adjuvant therapy. To achieve this, we designed a specific LNP formulation to serve as the carrier for the Cas13b RNP system. Our findings validate Cas13b RNP as a viable potential strategy to increase gemcitabine sensitivity in pancreatic cancer cells having a synergistic effect, and we are currently studying the use of LNPs to optimize the cell delivery of the system.

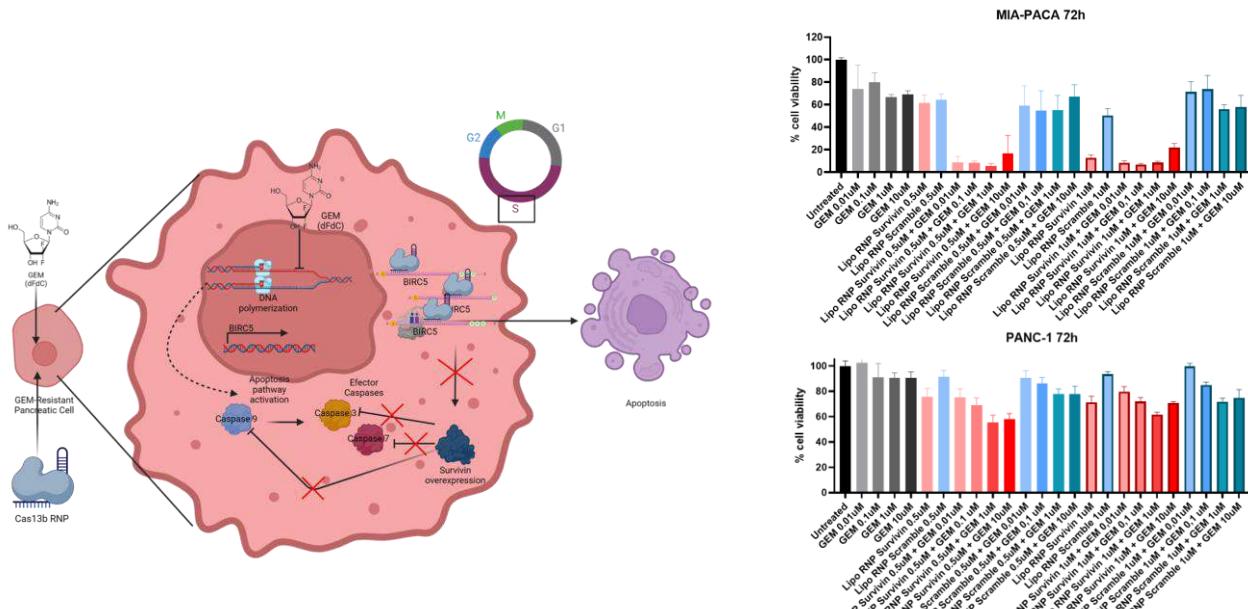


Figure 1. A Scheme explaining the combined theoretical action of Gemcitabine and Cas13b RNP (with a crRNA for BIRC5) in GEM-resistant cancer pancreatic cells. **B** Cell Viability of MIA-PACA and PANC-1 cells 72 hours after the treated with different concentrations of Gemcitabine and Cas13b RNP targeting BIRC5 mRNA.

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Study of the effect of Nanostructured Conductive Surfaces on Neural Differentiation

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Due to the limited capacity for neuronal regeneration, neurodegenerative diseases present a considerable challenge for the field of Regenerative Medicine. This work examines the application of nanostructured surfaces featuring grating topographies aimed at promoting neuronal orientation, extension, and differentiation through mechanotransduction processes. Additionally, Carbon Nanotubes (CNTs) have been incorporated to the topography to investigate the effects of electrical stimulation on the establishment of neuronal connectivity. To this end, polystyrene (PS) substrates were coated with a CNT dispersion through spin-coating, and the topographies including 416 nm gratings, 2 μm gratings, were subsequently patterned using Nanoimprint Lithography (NIL). These surfaces were meticulously characterized by Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). The differentiation of neuroblastoma-derived SH-SY5Y progenitor cells was studied on the different topographies following a 15-day culture period in the presence of retinoic acid. The cell's differentiation was assessed via SEM and immunofluorescence labelling with specific neuronal markers (MAP2, TUB3, and DAPI). Preliminary results reveal an enhancement in cellular differentiation on the 416 nm gratings and a marked cellular alignment on the 2 μm gratings, suggesting that these topographies, in conjunction with CNTs, may serve as a valuable tool to promote neural differentiation.

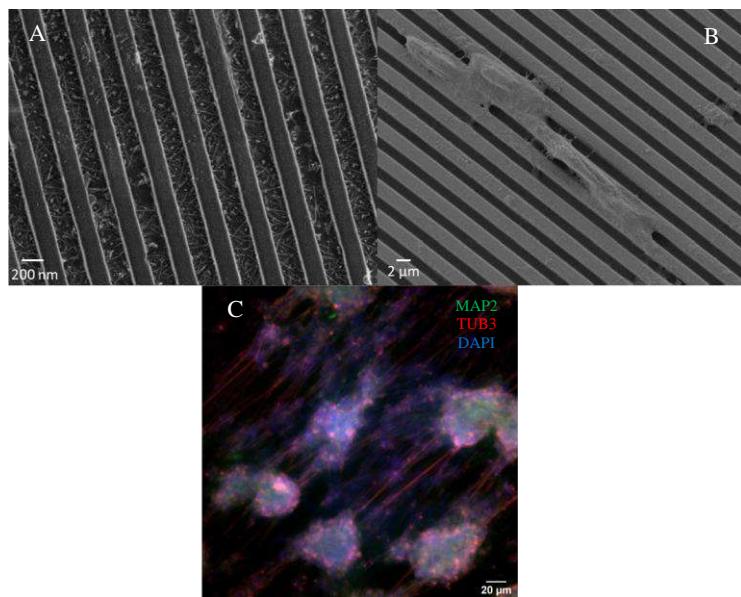


Figure 1. A) SEM of a PS surface with CNT and 416 nm gratings. B) SEM of SH-SY5Y cells differentiated for 15 days on a PS surface with 2 μm gratings. C) Immunofluorescence of SH-SY5Y cells differentiated for 15 days on a PS surface with 416 nm gratings (neuronal markers: MAP2 (green), TUB3 (red), and DAPI (blue)).

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USING QUANTUM DOTS AS BIOSENSORS TO IMPROVE ALS' PATHOLOGICAL PROTEIN ANALYSIS BY IMMUNOFLUORESCENCE.

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Nanoparticles have become highly promising tools in the field of biomedicine, particularly for their applications as biosensors. Among these, Quantum Dots (QDs), which are luminescent semiconductor nanoparticles, stand out due to their unique optical properties, such as a narrow emission spectrum, high brightness, and remarkable photostability¹. Additionally, their versatile surface chemistry enables efficient bioconjugation to a variety of biomolecules, allowing for the specific labeling of proteins and other cellular components of interest².

Because of these properties, QDs are becoming increasingly useful in the study of complex diseases, including neurodegenerative disorders such as Amyotrophic Lateral Sclerosis (ALS), Alzheimer's Disease (AD), and Parkinson's Disease (PD). ALS, a devastating and fatal neurodegenerative condition, is characterized by the progressive degeneration of motor neurons, leading to muscle paralysis and death. One of the key proteins implicated in ALS pathology is TDP-43, a protein with crucial functions in the nucleus, including RNA stabilization and mRNA transport. In ALS, TDP-43 undergoes abnormal aggregation in the cytoplasm, leading to the disruption of cellular homeostasis and contributing to the neurodegenerative process^{3,4}. Despite considerable efforts, effective treatments for ALS remain elusive, highlighting the need for further research into the molecular mechanisms driving the disease.

In a recent investigation, we studied the behavior of QDs in lymphoblasts and found that these nanoparticles are unable to penetrate the nucleus of cells, making them ideal for labeling cytoplasmic proteins. This property of QDs allows selective targeting of cytoplasmic proteins, such as TDP-43 and its phosphorylated form, in immunofluorescence assays⁵. Importantly, QDs can be used to track the aggregation and mislocalization of TDP-43 in ALS, providing insights into the pathological mechanisms associated with the disease.

In addition, with QDs we can simultaneously tag multiple targets within a single cell (Figure 1), allowing us to study complex protein interactions and cellular processes more comprehensively. This multiplexing capability enables a deeper understanding of the molecular pathways underlying ALS and, potentially, other neurodegenerative diseases.

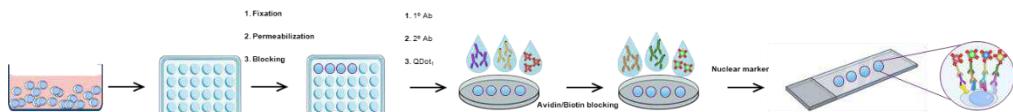


Figure 1. Graphical representation of multi-step immunofluorescence.

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Nanofabrication based on lithographic techniques for minimal-invasive neural interfaces

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Today, neurological disorders affect a significant percentage of the population, which is increasing due to a larger life expectancy and a higher popularity of risk sports. One of the most successful ways of studying and treating neurological disorders is the use of neural interfaces to record or stimulate neural activity. However, creating neural interfaces for long-term implantation still poses challenges, such as minimizing inflammatory response and ensuring durability [1]. Nanofabrication of electrodes for neural interfaces is an important field in neuroscience and biomedical engineering, which carries the promise of overcoming these challenges. Nanostructuring the electrode surface allows for more precise and minimally invasive interaction with neural tissues, which is important for improving both research and treatment.

In this work, our progress on the development of nanostructured electrodes for neural interfaces is presented. We combine optical lithography techniques with electrochemical processes, like electrodeposition. The main goal is to create a flexible implantable interface based in polymeric materials, with electrode pads of nanostructured surface with nanopillars. This nanostructure increases the effective surface area of the pads and reduces the impedance at the interface between the tissue and the electrodes [2]. To achieve this nanostructuring, we work with anodic aluminium oxide (AAO) and polycarbonate (PC) membrane templates. The process starts with the deposition of a polyimide layer over glass by spin-coating, followed by an optical lithography process, which has successfully allowed us to define gold microcircuits on a flexible device, which can easily be peeling off the glass substrate. We are now working on validating the strategy for nanostructuring the micrometer pads and optimizing electrochemical growth of gold using a lab prepared electrolyte.

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Ultrasound-induced Nanostructuring of a 3D Spin Crossover Metal-Organic Framework

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Metal-organic frameworks (MOFs) are highly versatile materials with customizable porosity, large surface area, and functional adaptability, making them suitable for various applications. However, their bulk form presents challenges for precise control and integration at smaller scales.^[1] Miniaturizing MOFs, particularly those exhibiting *Spin Crossover* (SCO) behaviour, is promising for enhancing their functionality in fields such as sensing, data storage, and molecular switches.^[2] SCO MOFs undergo a reversible transition between high- and low-spin states in response to external stimuli, but maintaining these properties at the nanoscale remains challenging. Innovative approaches are needed to preserve their structural integrity and physico-chemical properties while leveraging the unique benefits of miniaturization. In addition, understanding the crystalline structure of these nanocrystals is crucial for tailoring their properties to specific applications. **Nanocrystals** exhibit unique characteristics due to their reduced dimensions, whose interpretation requires precise knowledge of their atomic arrangement. **Micro-crystal Electron Diffraction** (MicroED) emerges as a revolutionary solution, offering unparalleled insights into nanocrystal structures at the atomic level. By harnessing electron diffraction at the microscale, MicroED provides high-resolution data, enabling the identification of bond lengths, angles, and defects. Moreover, its ability to analyse nanocrystals²⁶⁷ *in situ* without extensive sample preparation makes it invaluable for real-time observations of dynamic processes. Overall, MicroED plays a pivotal role in advancing nanoscience and nanotechnology by facilitating the design of nanocrystals with tailored properties and enhanced functionalities.

Herein, the synthesis of $[\text{Fe}_2(\text{H}_{0.6}\text{bdt})_3] \cdot 9\text{H}_2\text{O}$ nanocrystals (**I**_{nan}) has been carried out by sonication. This MOF is very interesting for its *nanostructuring* as it possesses not only spin transition but also conductivity, and the relationship between both properties has been previously demonstrated in single crystals.^[3] The characterization of **I**_{nan} was performed, mainly using SEM and AFM. Additionally, the crystalline structure of **I**_{nan} was obtained from MicroED and compared to that of the macrocrystals previously reported (**I**). Furthermore, the impact of the size reduction from the macroscale to the nanoscale on the physico-chemical properties of these crystals has been studied, mainly through Raman spectroscopy and electrical conductivity measurements. This exhaustive comparison between **I** and **I**_{nan} demonstrates the preservation of the crystalline structure in the nanoscale and the retaining of the properties of the material, validating the applicability of this approach for the miniaturization of 3D MOFs.

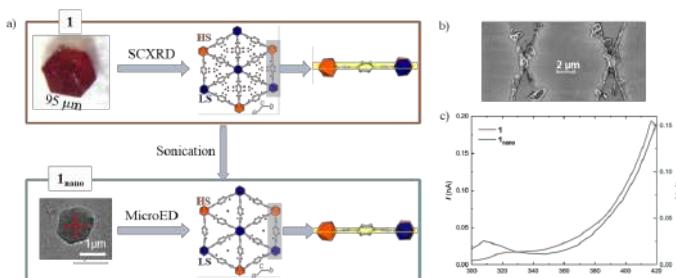


Figure 1. a) Schematic representation of the conversion from **I** to **I**_{nan}. b) SEM picture of the gold devices in which **I**_{nan} was trapped for the charge transport measurements. c) Current-temperature dependence of **I** and **I**_{nan}.

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Nanodiamonds enhanced electrochemical sensors for sensitive bisphenol A detection

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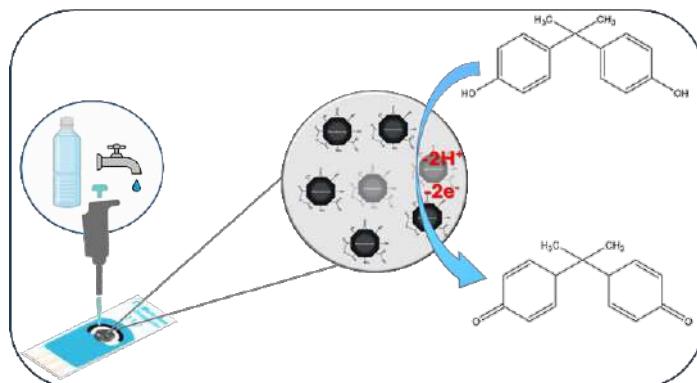
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This research work presents the development of a sensor platform using screen-printed carbon electrodes modified with nanodiamonds (NDs) for the electrochemical detection of bisphenol A (BPA), a harmful endocrine disruptor. The modification with NDs resulted in the formation of highly stable and conductive surfaces, thereby enhancing the performance of the sensors for water quality monitoring. Scanning electron microscopy (SEM) was used to confirm the nanostructured surface, while cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to characterize and optimize the detection process. The electrodes modified with NDs showed superior analytical characteristics compared to the unmodified electrodes, exhibiting higher current responses at lower potentials and preventing immediate fouling after BPA oxidation. Under optimal conditions, the sensor showed a linear relationship between signal intensity and BPA concentration up to 100 μM . The method demonstrated a limit of detection of 0.310 μM and a limit of quantification of 0.930 μM . Finally, the modified electrodes were successfully tested on tap and bottled water samples, demonstrating their practical utility for sensitive and reliable BPA detection in water from different sources. This reinforces the potential of NDs-modified electrodes in environmental monitoring.



Collapse of the Drude Model in Silicon at Low Temperatures

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At room temperature, Silicon's (Si) frequency-resolved complex conductivity can be accurately described by the Drude model for electrical conduction. However, experimental work has shown that the Drude model's capacity for properly describing the conductivity in the AC limit gets compromised at cryogenic temperatures [1-2], a behavior not clearly understood at the molecular level. In the present work, we revisit the topic aiming on elucidating the mechanisms behind this peculiar behavior.

To analyze this issue, we use Terahertz Time Domain Spectroscopy (THz-TDS) [3-4]. This non-contact spectroscopic technique has been proven to be a powerful tool for the exploration of the native state charge-carrier dynamics of materials in the dark, by directly accessing their frequency-resolved properties such as refractive index, permittivity and electrical conductivity. Our research focuses on the analysis of the electrical THz conductivity of B-doped p-type Si within the temperature range of 4 K to 300 K. Initially we obtain observations in agreement with those described earlier, finding that from 300 K to \sim 100 K the frequency resolved complex conductivity can be well described with the Drude model, while from \sim 100 K to 4 K the quality of the fit of the Drude model continuously decreases, until becoming truly inadequate at the very lowest temperatures. Our main finding is that the onset temperature where reliable Drude fits are not possible is clearly linked to the so-called "freeze-out" region, i.e., the temperature onset where free charge carrier density drop with temperature as thermal ionization of defects is quenched.

We are currently working on describing a new model for the frequency-dependent AC-conductivity at lower temperatures. This work may lead to a universal understanding of the mechanisms governing the native state charge-carrier dynamics of materials in cryogenic conditions and the exotic microscopic phenomena taking place.

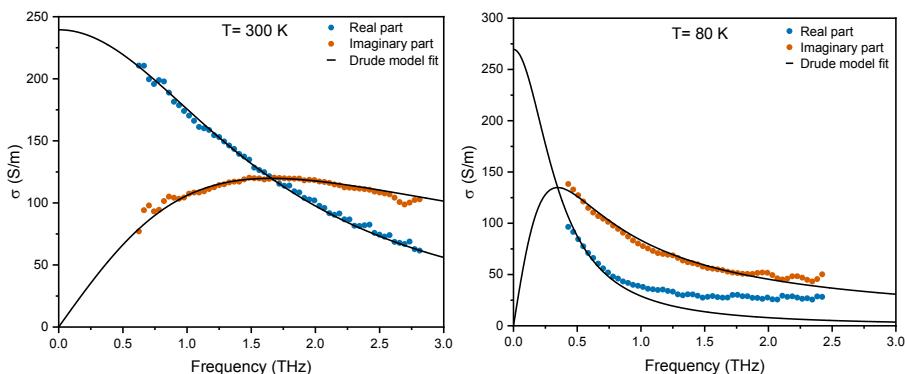


Figure 1. Frequency-resolved conductivity. Drude response can be observed at 300 K while the model considerably fails for temperatures below \sim 100K (example at 80 K).

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Copper-silver nanobiomaterials with antimicrobial properties

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The current emergence of antibiotic resistant bacteria has become a problem of global scale that requires the development of new materials capable of combating it. Among them, metal-based nanomaterials are a major focus of attention due to their proven antimicrobial effect and their peculiar mechanisms of action [1,2]. There are several methods to obtain them, and a novel synthesis strategy consists of generating new nanomaterials by using an enzyme as an inducer.

In this study, the development of copper-silver bimetallic nanomaterials is proposed, evaluating the effect of the synergy between both metals in their efficiency and their antimicrobial properties. The different bimetallic hybrids were designed adding different silver concentrations (from 12 to 0.6 mg/mL) to a previously designed copper nanomaterial with good antiviral activity [3,4].

The new nanobiomaterials were fully characterized and their antimicrobial efficacy was tested against different bacterial and virus strains. The antimicrobial performance of the Cu-Ag hybrids against *Escherichia coli* resulted in greater inhibition values compared to the only copper hybrid, achieving a 4 log reduction in the bacterial population with the best of them (5%Ag-Cu-CALB) [5]. Then, the antiviral capacity of 5%Ag-Cu-CALB hybrid was tested against the human coronavirus 229E and the human rhinovirus HRV-14. Results demonstrated its also efficient antiviral capacity, with more than 3 log of inhibition against HRV-14.

These results suggest that the incorporation of an small amount of silver into a copper nanobiohybrid creates a new nanomaterial with enhanced antimicrobial capacity and open up the possibility of developing new advanced materials that could help combat a variety of health concern pathogens.

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Aqueous Two-Phase Extraction for the Sorting of Mechanically-Interlocked Derivatives of SWNTs

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Discovered over three decades ago, single-walled carbon nanotubes (SWNTs) have captivated researchers due to their exceptional properties, including remarkable electrical and thermal conductivity, mechanical strength, and suitability across diverse fields.¹ Among those extraordinary properties, SWNTs can be chiral depending on the pitch of the vector along which the constituting graphene sheet is folded. The (n,m) indices specify the nanotube's diameter and influence its electronic characteristics, with certain chiralities resulting in metallic behavior and others yielding semiconducting properties with well-defined bandgaps. Additionally, for each semiconducting type and for metallic nanotubes that are not armchair configurations, both right-handed and left-handed helical structures are formed. To fully exploit the properties of SWNTs, their functionalization and separation is required.

As an alternative to the conventional covalent bonding and supramolecular approach to functionalize SWNTs, in 2014, we reported a novel approach to functionalize SWNTs through the formation of mechanically interlocked nanotubes (MINTs).² This type of functionalization combines the stability of covalent modifications with the structural integrity, characteristic of non-covalent interactions. That is, it results in very stable products without altering the structure of the SWNTs.

For the separation of SWNTs, different techniques have been applied such as gel chromatography, density gradient ultracentrifugation (DGU) or aqueous two-phase extraction (ATPE). Traditionally employed in the biological field, ATPE technique is being applied to SWNTs as a powerful method for sorting the different species present in synthesized samples.³ The aim of this work is to extend this technique to MINTs, addressing the challenge of purifying mixtures of non-functionalized (pristine SWNTs) and functionalized nanotubes (MINTs), which exhibit a wide range of functionalization. By refining the ATPE process, efforts are focused on exploring its potential for purifying and sorting MINT species based on their functionalization levels, chirality, and enantiomeric properties. Comparative studies on standard and chiral MINTs aim to uncover the versatility of this technique in isolating distinct characteristics of these novel materials. To evaluate the effectiveness of these efforts, a range of analytical techniques is employed, including UV-Vis-NIR and photoluminescence excitation spectroscopies, Raman spectroscopy, and circular dichroism. Comparative studies of standard and chiral MINTs aim to demonstrate the versatility of ATPE in isolating and characterizing these novel materials. These findings will help pave the way for MINT applications in a wide array of innovative technologies.

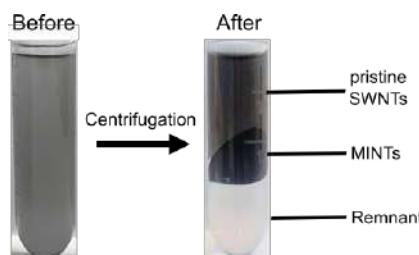


FIGURE. Purification and Sorting of MINTs.

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Multiple Post synthetic modification over 3D MOF europium metal center

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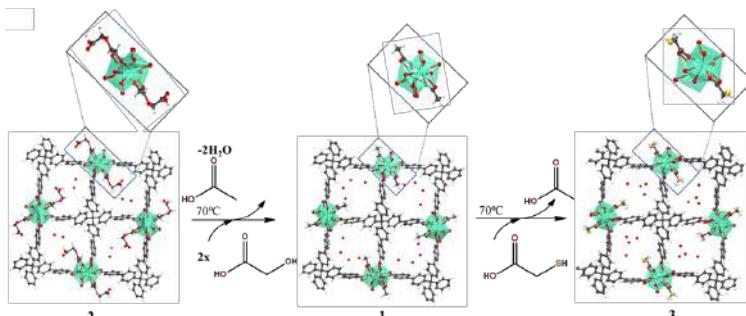
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Metal-organic frameworks (MOFs) are crystalline compounds in which metal nodes are linked in infinite arrays via multitopic ligands. This crystalline solids with accessible open spaces have rapidly become an important area of chemical research, engaging the interest and excitement of a broad community in the last two decades¹. Coupled with the advances in synthesis and functionalization of MOF, post-synthetic modifications (PSM) are a powerful strategy to modify their physical properties or provide them with new chemical characteristics, without altering the overall framework, and also to prepare MOFs with functionalized pores. PSMs on MOFs are transformations or exchanges performed on pre-synthesized MOF materials by introducing functional groups or molecules². In this work, we report a robust and stable 3D metal-organic framework based in lanthanide metallic center with carboxylate ligands and coordinated acetic acid molecules. These acetic acid groups undergo conversion by diffusion of two organic acids into the structure, resulting in modification of the MOF on the europium metal center, giving rise two new compounds, **2** and **3**. This synthetic approach allows for post-synthetic functionalization of the MOF and is a powerful, fast, and versatile method to prepare tailor-made functional MOFs in a straightforward manner. In moreover, further post-synthetic reactions would be possible on these new acids, which could be used for a broad variety of applications.

Figure 1. Post-synthetic modifications of **1** through reaction with glycolic acid (**2**) and thioglycolic acid (**3**).



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Concomitant Thermochromic and Phase-Change Effect in a Switchable Spin Crossover Material for Efficient Passive Control of Day and Night Temperature Fluctuations

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Nowadays, building thermalization is a widespread human necessity, accounting for 28% of energy-related carbon dioxide (CO_2) worldwide emissions.^[1] These CO_2 emissions are a major contributor to climate change, which has become one of the biggest concerns of humankind.^[2] Thus, the growing energy-saving and environmental protection demand have prompted the development and implementation of more energy efficient and environmentally friendly thermalization technology. In this regard, remarkable efforts have been focused on the implementation of passive thermal regulation systems, that can be incorporated directly into windows,^[3] roofs, or walls of buildings and operate without the need for electricity.^[4]

Here, it is demonstrated that the heat generated by the sun is sufficient to produce a partial spin transition in an spin crossover (SCO) material. SCO materials exhibit a reversible transition, between the high spin and low spin electronic states through the application of external stimuli such as temperature.^[5] This SCO leads to a cooling effect with respect to other materials, due to an increase in light reflection resulting from the color change (from pink to white) and the energy absorption associated with the spin transition. In addition, when the material is cooled, a dampening of the temperature decrease is produced due to the energy release associated with the spin transition. Therefore, these materials can be used to reduce temperature fluctuations, and could potentially be implemented for passive temperature control in buildings. Interestingly, SCO molecule-based materials are remarkably stable upon cycling and highly versatile, allowing for the design of compounds adapting the intended properties (transition temperature and hysteresis) for the desired climatic conditions and comfort temperature.

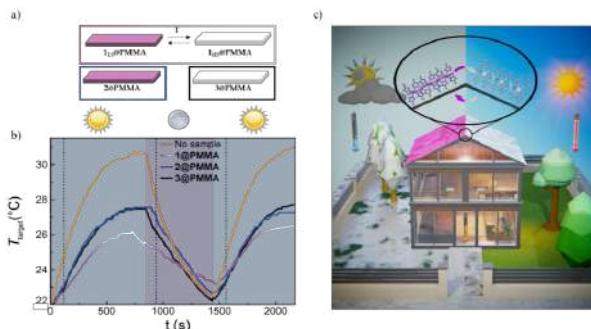


Figure 1. a) Compounds employed in the experiment: 1 (that displays a spin transition associated with a change of color between white at high temperatures and pink at low temperatures), 2 (pink) and 3 (white). b) Temperature in the sensor vs. exposure time with on-off solar simulator cycles. c) Illustration of the working scheme.

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Efficient CO₂ optical sensor based on europium 3D MOF/PDMS composite

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Nowadays, the increasing concentration of Green House Effect gases (GHGs), and specially, carbon dioxide due to anthropogenic activities has led to concerns about global warming, climate change, and health impacts. Therefore, the detection and monitoring of CO₂ levels are of paramount importance in various domains, including environmental monitoring, industrial process control, and indoor air quality management. So on, the development of effective and reliable CO₂ sensors will be one of the most important challenges for the upcoming generations [1], [2]. Herein, the synthesis and physicochemical characterization of a 3D porous luminescence europium-based MOF for the efficient detection and straightforward quantification of CO₂ molecules have been described.

Exposure of the porous structure to CO₂ triggers a fast Eu³⁺ luminescence intensity increase, which is fully reversed upon inert gas purging at room temperature, a process that can be repeated several times without signs of hysteresis, demonstrating the compound's high robustness. Furthermore, the compound was successfully embedded in a PDMS matrix, resulting in a composite material that exhibits a similar luminescence intensity profile to the original compound when exposed to CO₂, but with even better results. All these results reveal that this compound is a promising candidate for the design of future reusable luminescent sensors for some atmospheric pollutants.

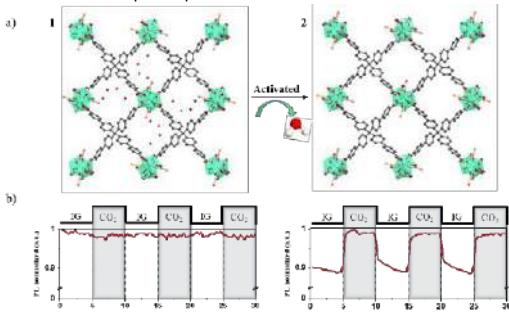


Figure 1. a) Crystalline structure of **1** (on the left) and **2** (on the right, after activation, without solvents) along c axis. b) The PL response of **1** (on the left) and **2** (on the right) to CO₂ after activation following exposure to three consecutive inert gas/CO₂ cycles. The time interval for each exposure was 5 minutes.

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Dual-action hydrogel with anti-inflammatory and antibacterial properties with a salicylate-exchanged ionic liquid

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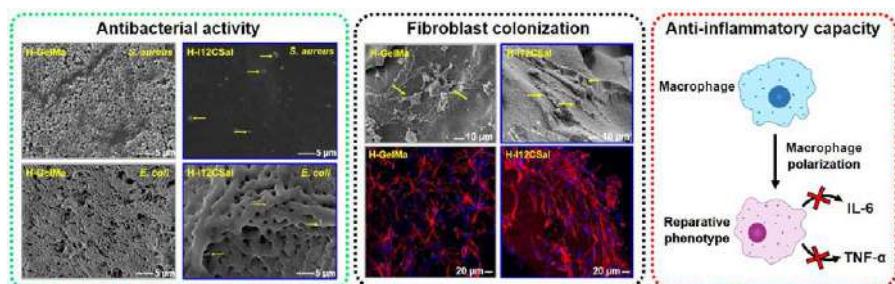
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Infections are becoming a principal cause of mortality as a consequence of the emergence of bacterial resistance mechanisms to conventional systemic antibiotic therapies. Local treatments can assist in addressing this issue by reducing systemic exposure and delivering antibacterial drugs directly to the wound site¹. This approach can be particularly advantageous in the treatment of skin wounds, where gelatin-based hydrogels have been proposed as a promising alternative therapy².

In this context, ionic liquids are becoming increasingly recognised as a novel antimicrobial therapy that offers an alternative to traditional antibiotics. Polymeric ionic liquids (PILs) combine the advantages of polymers and ILs³. These molecules are constituted by a cationic moiety possessing antibacterial properties and an anion, typically bromine, iodine or chlorine, which can be substituted with a bioactive alternative.

In this work, we present a gelatin methacryloyl-based hydrogel incorporating an antibacterial PIL into its structure. The anion was exchanged with sodium salicylate, which confers anti-inflammatory properties. The physicochemical properties of the hydrogels were characterized by evaluating their swelling capacity, rheological behavior, and degradability. The colonization of the material by mouse endothelial fibroblasts confirmed its biocompatibility. A flow cytometry assay was performed to assess the anti-inflammatory effect, and showed the differentiation of mouse macrophages to a reparative phenotype. The levels of pro-inflammatory cytokines (IL-6 and TNF-α) were reduced compared to the control material, fully confirming the anti-inflammatory effect. The antibacterial activity was evaluated and showed great results against both *Escherichia coli* and *Staphylococcus aureus*. These findings indicate that this biomaterial may be useful as a wound dressing for the infected tissue injuries.



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Acknowledgments

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Development of sensors based on doped carbon nanodots for the detection of biomarkers associated with respiratory ailments.

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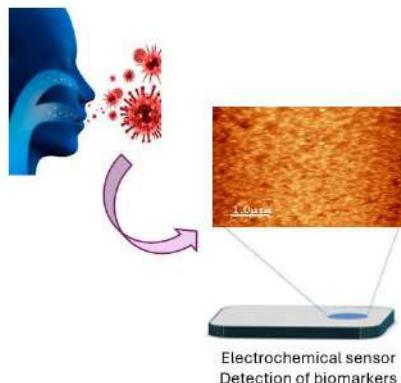
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The development of sensors using doped carbon nanodots is an advanced area of research focused on improving environmental and practical efficiency. This study aims to create a sensor for the quick screening of patients with respiratory conditions. Initially, the emphasis is on designing these sensors with doped carbon nanodots, with *methyl nicotinate*—a tuberculosis indicator being the primary analyte examined. An efficiency analysis was conducted for the catalysis of this analyte, and, after identifying the most efficient carbon nanodot type, the stability of the sensor was assessed. The most effective carbon nanodot found was enriched in nitrogen atoms but undoped with metals or metalloids.



Design and synthesis of a molecular nanographene exhibiting sharp aggregation-induced emission

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The synthesis of a new molecular nanographene para-hexa-peri-hexabenzocoronene-tetraphenylethene (TPE-HBC) (Figure 1a) has been carried out from two staple compounds in the same system, namely: tetraphenylethene (TPE) and hexa-peri-hexabenzocoronene (HBC). The synthetic path has been designed to obtain a core system composed by the TPE functionalised with diphenylacetylene, where the acetylene group acts as a reactive centre for the formation of the HBC moiety. The synthetic path consists in six reaction steps and the obtained compound has been characterized by standard spectroscopic and analytical techniques.

Interestingly, it has been observed that the prepared TPE-HBC shows the aggregation-induced emission (AIE) phenomenon like other similar compound recently reported in our group, the tetrahedraphene.¹ Therefore preliminary studies of emission in THF/H₂O mixtures have been carried out. In Figure 1b, the AIE process is shown, finding that keeping unaltered the concentration of the TPE-HBC and varying the ratio of the good solvent and the anti-solvent, the luminescence changes (Figure 1c). With a high concentration in THF (good solvent), the luminescence spectrum appears similar to that of single HBC, namely a sharp peak at about 475 nm and another one at 500 nm. Increasing the quantity of water (anti-solvent) it is possible to observe a bathochromic shift of the peaks. In fact, at a low concentration in THF, a larger and more intense band at about 580 nm is observed. Therefore, a new and promising molecular nanographene has been synthesized with remarkable AIE properties.

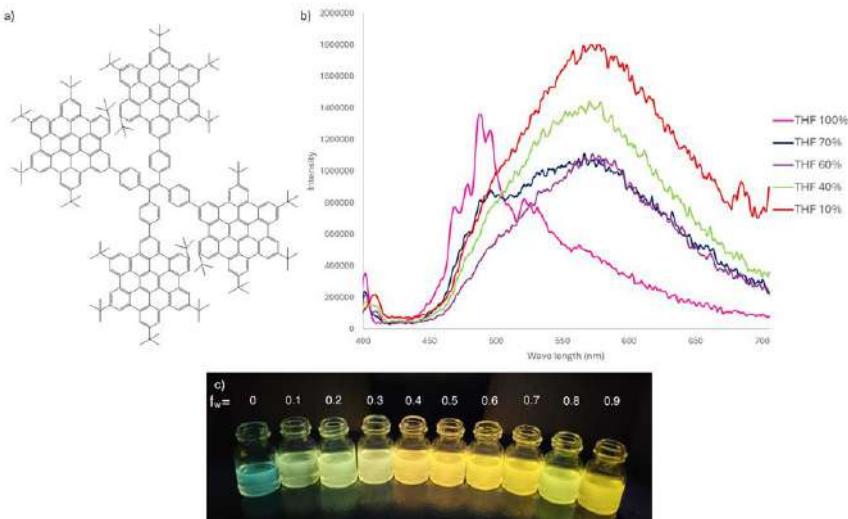


Figure 1. a) Chemical structure of new TPE-HBC; b) Emission spectra TPE-HBC in THF/H₂O mixtures at 1×10^{-6} M; c) Variation in the colour emission upon UV lamp irradiation

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Abstract:

Molecular electronics has emerged from the need to characterize and study electron transport at the single-molecule level. The importance of being able to measure one or a small number of molecules lies in the possibility of mimicking the behavior and functionality of basic electronic components at the nanoscale, such as wires, potentiometers, switches, and more. The miniaturization of these electronic devices has given significant relevance to molecular electronics research in recent years, especially with the development of the scanning tunneling microscopy break-junction (STM-BJ) technique. Through STM-BJ, it is possible to measure the conductance of one or several molecules positioned between two metal electrodes. [1] Results obtained using this technique have increased the understanding of molecules' electrical properties and the influence of each molecule's structure on electron transport. Molecular electronics greatly benefits from the field of organic chemistry, which allows the synthesis of molecules with specific structures to replicate the behavior of certain electronic components, as well as from the use of STM-BJ, which facilitates the study of these molecules' conductivity. However, a primary objective remains to control the oxidation state of the studied molecules, as their electronic properties can be affected by their oxidation state.

The aim of this work is to implement the necessary changes into our homebuilt STM-BJ systems to conduct measurements of molecules under electrochemical control. Achieving these modifications would not only allow for monitoring and controlling the oxidation state of molecules under study but could also extend the use of electrodes to non-noble metals, such as Ni. Currently, efforts are focused on adapting the previous STM-BJ setup, by adding a bipotentiostat to independently control the currents of the tip and substrate, as well as a small cell that allows the introduction of new elements: the electrolyte solution, the counter-electrode, and the reference electrode. These modifications provide a valuable approach for obtaining insights into metal-molecule interactions and studying the electrical properties of molecules under electrochemical control, thereby advancing the design of new nanometric-scale electronic devices.

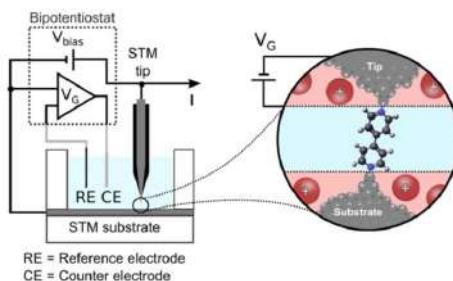


Diagram of a four-electrode-based EC-STM. Adapted from Brooke et al. [2]

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Covalent Organic Frameworks as emerging catalysts

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Covalent organic frameworks (COFs) are a class of crystalline, porous, and organic polymers connected by covalent bonds (Figure 1A). These materials displays an hierarchically organized structures with predictable control over the structural features at the nanoscale.¹ J. L. Segura's research group is dealing with the synthesis of COFs for the obtainment of novel catalysts including: novel photocatalysts for C-H functionalization reactions, and CO₂ reduction reaction (CO₂RR) or oxygen reduction reaction (ORR) electrocatalysis.²⁻⁷ These electrocatalysts are often produced by top-down processing of the bulk COF by liquid phase exfoliation to obtain covalent organic nanosheets (CONs) to modify glassy carbon electrodes (GCE) (Figure 1B). Thus, the crystalline nature of the organic frameworks allows the study of structural-property relationships, such as the pathway selectivity of the ORR (two- or four-electron reduction), which has emerged as a powerful tool for H₂O₂ *in situ* production or the assembly of fuel-cells. In this communication we will highlight our recent results concerning the design and method for the development of COF-based electrocatalysts and the dependence of the electrocatalytic response with the active site employed, modulating the electronic pathway and/or the performance (Figure 1C).

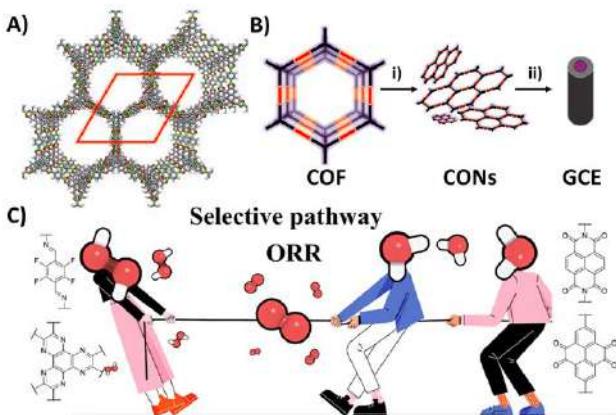


Figure. A) Structure of a COF. B) Workflow towards COF-based electrocatalysts (i) Exfoliation and ii) Drop-casting). C) Cartoon-representation of the different electronic pathways of ORR (left H₂O₂; right H₂O) and the active sites employed by our group.

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ATOMISTIC SIMULATIONS OF CRYOGENIC EXFOLIATION OF STERICALLY FRUSTRATED ATROPISOMERS SYNTHESIZED ON Au(111) SURFACE

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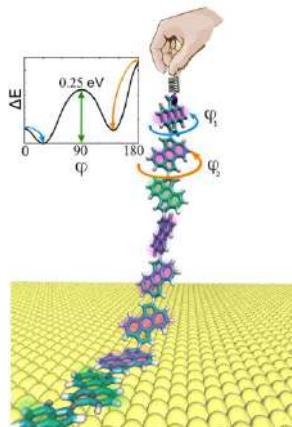
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On-surface synthesis enables precise bottom-up design of nanoarchitectures with strong covalent interactions¹. Notably, it imposes a 2D restraint on reactants, stabilizing unique conformations that are rarely observed in gas phase. This is especially relevant for atropisomers, molecules hindered in torsion rotation, where pharmaceutical protocols are yet to be established despite their significance in drug development. Recent studies using Scanning Probe Microscopy under cryogenic conditions together with Molecular Dynamics (MD) simulations have provided insights into the mechanical and tribological properties of polymeric chains on surfaces^{2,3}. This research focuses on weakly atropisomeric poly-aromatic-hydrocarbon (PAH) chains, employing nanomanipulation with cryo-force spectroscopy and MD simulations to analyze and stabilize them. The research observes strong stability in the contiguous configuration of different monomers – parallel or antiparallel – even after detachment and redeposition. This investigation contributes valuable insights into the mechanical behavior and structural stability of PAH molecular chains synthesized on surfaces.



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Superconducting properties of highly corrugated Nb thin films

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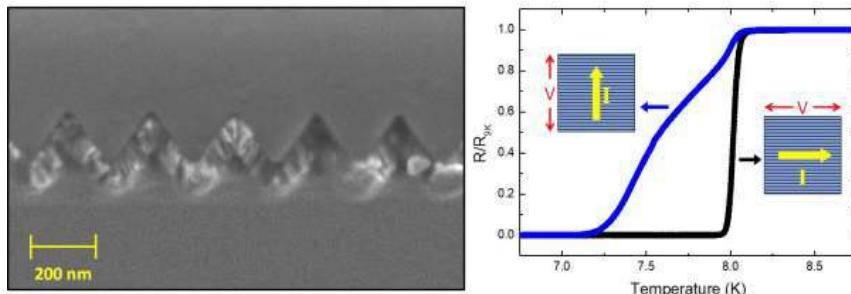
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Superconductors are present in a broad range of technologies requiring the generation of high magnetic fields and have also been proposed for applications in sensing, energy storage and non-conventional electronics. Nanoengineering is often required to improve the performance of such devices or allow the integration in novel architectures like those required in quantum computing. Other than traditional 1D (straight nanowires) and 2D (thin films) structures, 3D nanostructures shows interesting features [1] which could be convenient in the design of these new complex architectures.

In this work we study niobium, a type II superconductor, thin films grown on top of a patterned silicon substrate. The film is conformal with the triangular pattern, resulting in a highly corrugated surface with a well defined geometrical symmetry. Low-temperature electrical transport measurements were carried out in this system, showing a superconducting transition whose shape noticeably depends on the direction of the applied current.



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Electrical characterization of a large-area single-layer of Cu₃BHT 2D conjugated coordination polymer

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Two-dimensional conjugated metal-organic frameworks (2D c-MOFs) are formed by the coordination of metal centers and planar organic conjugated building blocks. The modular nature of 2D c-MOFs make them highly advantageous for realizing materials with extensive tunability of their electrical and optical properties. In this contribution, I will discuss the synthesis and electrical characterization of a large-area, single-layer Cu₃BHT 2D MOF. The Cu₃BHT layer was synthesized at the water surface using the Langmuir-Blodgett technique and subsequently transferred onto SiO₂/Si substrates with pre-patterned electrical contacts. Electrical measurements displayed ohmic behavior across areas as large as ~1 cm². Cooling and heating cycles revealed hysteresis in the electrical response, indicating the formation of different current pathways as the samples underwent structural and chemical changes during the temperature sweeps. This hysteresis diminished after several cycles, with the conductivity stabilizing into an exponential temperature dependence, suggesting a tunnelling process governed the conduction mechanism in these polycrystalline single-layer Cu₃BHT samples.

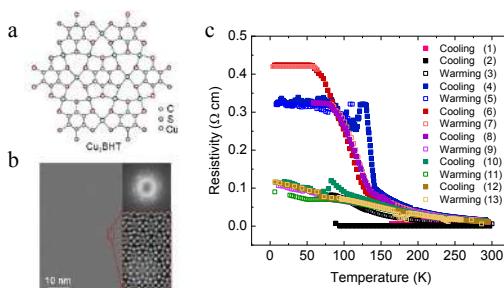


Figure: a. Schematic structure of Cu₃BHT. b. AC-HRTEM image of Cu₃BHT. c. Resistivity-temperature of a single-layer Cu₃BHT sample during different temperature cycles. The numbers in parentheses indicate the order in which the measurements were conducted.

Note:

The paper was accepted to be published in the journal of Advanced Functional Materials.

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Binder-Free 3D Printing of Metal-Organic Polyhedra Aerogels

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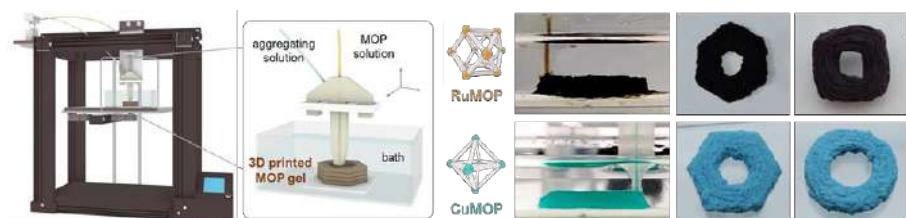
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Interest in producing functional materials through 3D printing has grown significantly over the past few years, owing to its ability to fabricate objects with precise shapes and dimensions, which enables better adaptation to specific requirements [1]. In the field of porous materials, researchers have recently explored the 3D printing of metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), with early efforts using binders to facilitate the process [2,3]. However, these binders often decrease the porosity of the printed composites, prompting a shift towards binder-free inks to fully utilize the material's porosity. In that sense, we recently reported a novel approach exploiting the gelation of a 3D printable ink based on a colloid of COF nanoparticles, together with a microfluidic device to control the gelation process [4]. Nonetheless, formulating these additive-free inks still remains a challenge, as the materials must be synthesized as nanoparticles with precise control over size and surface properties, all while ensuring the formation of stable colloids.

In this context, metal-organic polyhedra (MOPs) offer a promising alternative. MOPs are discrete porous coordination compounds, whose synthesis enables control over their surface chemistry and allows for adjusting their physicochemical properties such as solubility, reactivity, and stability [5]. Unlike insoluble MOFs and COFs, MOPs can readily form stable solutions through simple dissolution, facilitating easier and more controllable processing into inks. However, despite these appealing features, the potential use of MOPs for 3D printing remains largely unexplored.

Thus, in this communication we demonstrate the processing of MOPs into binder-free porous monoliths through 3D printing. We selected two MOPs capable of forming supramolecular gels, $[Ru_{24}(OH-bdc)_{24}]BF_4]_{12}$ and $[Cu_{12}(Ile-NDI)]_{12}$, each with different geometry, composition, and gelation mechanism. We optimized the conditions to precisely control the gelation process inside our microfluidic reactor, which acts as the nozzle of the 3D printer and allows layer-by-layer manufacturing. The obtained shaped gels are then converted into monolithic aerogels through supercritical CO_2 drying, creating self-standing MOP monoliths with complex shapes from computer designs. This study presents an important alternative for manufacturing structured micro/mesoporous materials by 3D printing, taking advantage of the unique properties of MOPs and holding promise for the preparation of mixed-MOP monoliths with spatial control over the composition of the printed monoliths.



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Quality or quantity? Unraveling the role of calcium in the osteogenic behavior of mesoporous bioactive glass nanoparticles

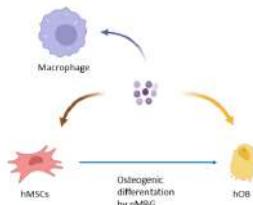
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Bioactive materials has emerged as a promising therapeutic strategy to address bone-related diseases.^[1] Due to their chemical composition, calcium-containing bioactive glasses, such as mesoporous bioactive glass nanoparticles (nMBG), have consistently demonstrated strong bone-regenerative potential.^[2] However, the impact of the Si/Ca ratio on the osteogenic properties of these nMBGs has not been thoroughly elucidated. In this work, we conducted a comprehensive physicochemical and biological evaluation of Si/Ca blends, with calcium content ranging from 10% to 40% (w/w). Our results indicate that increasing calcium content weakens the silicon framework, thus altering the ion release profile and changing the osteogenic potential. Protein corona analysis in human serum showed that protein patterns change with changes in Si/Ca ratio and duration of incubation. Cellular studies showed that certain calcium concentrations favor osteogenic differentiation, but that additional calcium does not enhance this effect. Recognizing these trends is essential to avoid misinterpretations of osteogenic activity without corroborative gene expression data. Finally, given the critical role of the immune system in tissue regeneration, the effect of nMBGs on immune responses was evaluated.^[3] We found that calcium-containing nMBGs favor macrophage polarization toward the M2 phenotype, highlighting their potential as bone regenerative nanomaterials.



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On-Surface Synthesis of π -Extended Subphthalocyanines

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In past decades, on-surface synthesis (OSS) has emerged as a powerful tool to prepare 2D materials from simple building blocks bearing reactive groups (e.g., halogen atoms).¹ If these building blocks present a bowl-shaped –rather than flat– structure, the peripheral (reactive) groups would be oriented toward the surface when a bowl-down configuration is adopted (Figure 1).^{2,3} This orientation is expected to influence the electronic and structural properties of such substituents. Based on this premise, an open question arises: could the bowl shape affect to the on-surface behavior of organic molecules, potentially activating bonds that typically exhibit poor reactivity? We have recently found that SubPcs, well-known contracted porphyrinoids, exhibit the aforementioned bowl-down configuration on Au (111), rendering them ideal molecular models to study the concept of "shape-assisted" on-surface chemistry.³

Here, it is demonstrated that SubPcs serve as excellent starting materials for the "toposelective" preparation of 0D and 1D curved π -systems (Figure 1). Remarkably, the size, shape, or even chemical nature (covalent or metalorganic) of the resulting product depends on the halogen used in the on-surface Ullmann coupling. Going one step further, the on-surface reactivity of SubPcs peripherally functionalized with groups that, in principle, are expected to be inert toward Ullmann-type C-C coupling (e.g., fluorine atoms), is described, revealing that shape matters on the on-surface reactivity of SubPcs.

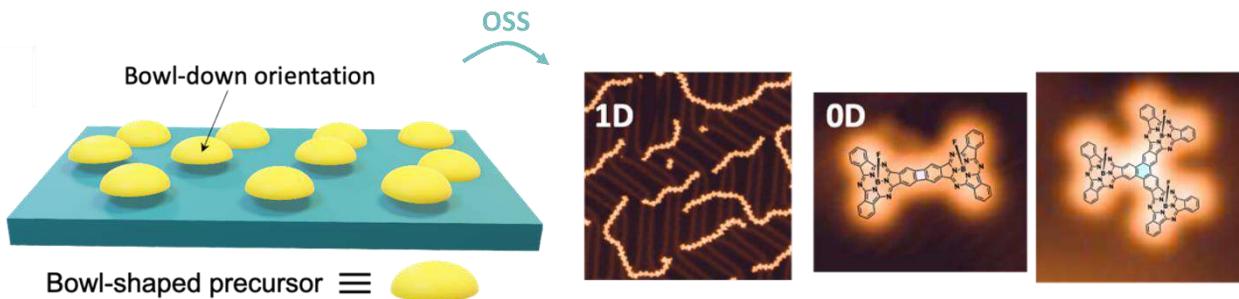


Figure 1. On-surface synthesis of 0D and 1D curved π -systems.

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Application of magnetic nanoparticles obtained by recycling of industrial steel residues in CWPO

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Reusing waste generated during product manufacturing is crucial to reducing environmental impact and maximizing resource efficiency [1]. Magnetic nanoparticles (NPs) can be used in diverse technological applications, one of them being addressing the pressing issue of pollutant removal from wastewater. The small size of these NPs allows for easy dispersion in liquids, and due to their large surface areas, they present a significant potential to interact with pollutants. Their magnetic properties might facilitate the NPs recovery [2].

This study shows results obtained applying a novel process that enables the transformation of steel industry residues into iron oxide NPs. The precursor was provided by CELSA Group in the form of powder with micrometer size particles. In view of the potential industrial scalability of the process, a physical method based on application of short milling times (IMDEA's self-developed "flash-milling" method [1,3]) has been used, followed by an optimized heat treatment. This route has enabled to move from a residue with a saturation magnetization (M_s) of 23 emu/g to iron oxide NPs with a M_s close to 130 emu/g after milling (10 min) and reductive annealing. The magnetic NPs obtained have been tested for the degradation of tebuconazole by catalytic wet peroxide oxidation (CWPO) [4], showing a degradation of more than 75 % of the pollutant in the first minutes of reaction, and apparent complete degradation after 90 min. Notably, the material showed outstanding stability, with limited dissolved iron concentration at the end of the reaction (0,0098 %Fe wt.).

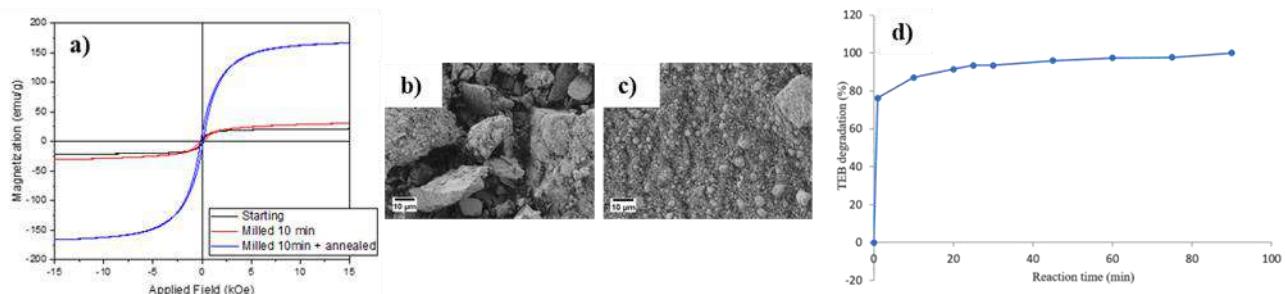


Figure 1: (a) Room temperature hysteresis loops measured by vibrating sample magnetometry (VSM) for the precursor powder and that after milling for 10 min before and after annealing. Scanning electron microscopy (SEM) images of (b) the starting powder and (c) the powder milled for 10 min. (d) Percentage degradation of tebuconazole during a CWPO process using the NPs as catalyst.

Acknowledgments

Authors acknowledge provision of the precursor material by CELSA Group and financial support through a CELSA-IMDEA Nanociencia collaboration project. IMDEA Nanociencia thanks support from the "Severo Ochoa" Programme for Centers of Excellence in R&D (MICINN, Grant CEX2020-001039-S), Comunidad de Madrid through NANOMAGCOST project (Ref. S2018/NMT-4321) and MICINN through the project NEXUS (PID2020-115215RB-C21). UAM thanks support from MICINN through the projects PID2019-105079RB-100 and PID2022-139063OB-I00.

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Nonlinear coherent diffractive XUV/X-ray imaging in quantum materials

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The emergent behaviour of quantum materials results from their complex electron dynamics at the nanoscale. Understanding these dynamics at their characteristic length and timescales thus requires nanoscale and ultrafast probes. To study spatial and temporal dynamics in solid state systems, coherent X-ray imaging techniques like Fourier transform holography (FTH)¹ and coherent diffraction imaging (CDI) are currently widely used², but various types of interactions do not manifest directly in the absorption of X-rays. Conversely, nonlinear wave mixing can reveal mechanisms that are hidden in conventional ultrafast XUV/X-ray spectroscopy, and have been applied to investigate the temporal dynamics of core-excitons^{3,4}, but without nanoscale spatial resolution. In order to combine nonlinear wave mixing processes with coherent imaging techniques, the new spectral content generated from wave mixing processes must be separated from the incidence XUV/X-ray absorption spectrum.

In this work we propose a novel coherent XUV/X-ray imaging method to study various nonlinear wave mixing processes using our newly developed analysis technique named coherent isolated diffraction imaging (CIDI)⁵. In the presence of nonlinear wave mixing in FTH, newly generated spectral component does not interfere with transmitted beam through reference holes due to energy mismatch and appears as an offset intensity on the diffraction pattern. CIDI analysis is capable of separating out the non interfering nonlinear components from the whole diffraction pattern and extract spatial and temporal evolution of nonlinear wave mixing in nano-scale. This technique provides the opportunity to study the dynamics of nanoscale pattern of nonlinear wave mixing, only limited to camera resolution, background noise floor, and coherence of the incidence beam.

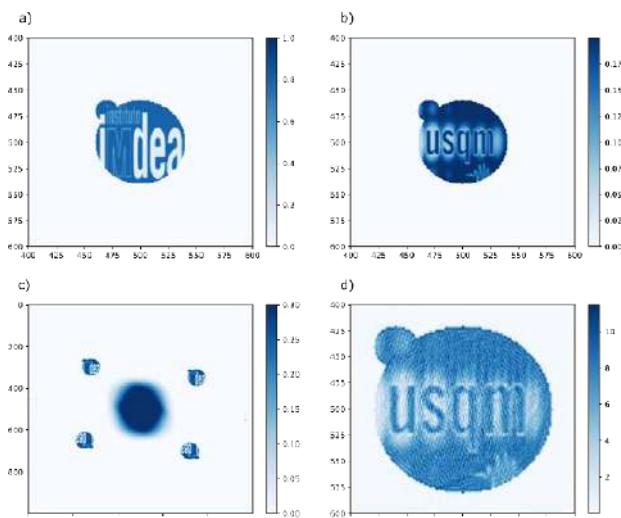


Figure 1: a) Absorption image and b) quadratic nonlinear pattern of a 2d sample used for numerical analysis. c) FTH image of the sample. d) Retrieved nonlinear pattern after imaging.

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Unveiling the inter-layer interaction in a 1H/1T TaS₂ van der Waals heterostructure (Oral contribution)

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1H/1T-TaS₂ heterostructures were first studied in 4Hb-TaS₂ crystals in the decade of the 90s [1], but the interest in them is now renewed due to the role played by doped 2D Mott insulators in the development of high Tc superconductivity in cuprates [2]. This highlights the need for a deeper understanding of the interactions between different 2D-layers in van der Waals heterostructures. In this work we study a 1H/1T heterostructure on a 2H-TaS₂ crystal by means of low temperature STM, scanning tunnelling spectroscopy (STS), Kolibri non-contact atomic force microscopy (NC-AFM) and first-principles calculations. We explore the transparency of the metallic 1H layer to the charge density wave (CDW) of the underlying Mott insulating 1T layer. This transparency effect is illustrated in Fig. 1, where we observe that the 1T-CDW is clearly resolved on a 2H/1T surface (panel a) superposed to the 1H-CDW (panel b) with a strongly bias dependent intensity (panel d) that follows the position in energy of the Upper Hubbard sub-band of the 1T layer underneath (panel c). From our results, it becomes clear that the conventional explanation relying on direct tunneling effect proves insufficient in explaining the observed transparency effect. We propose an alternative interpretation based on the hybridization between the electronic bands of the 1T and 1H layers.

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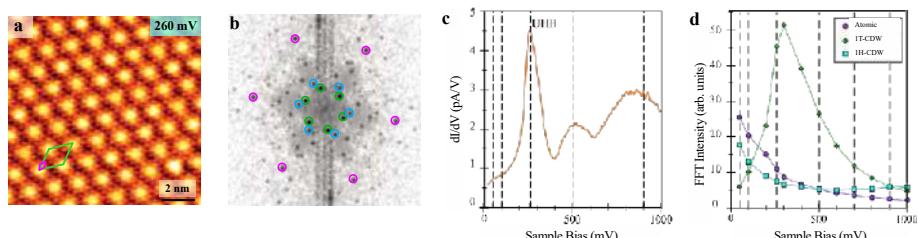


Fig.1 Transparency effect in STM: a) STM Image of a 1H/1T-TaS₂ crystal, where two periodicities are marked, in purple the atomic lattice and in green the 1T-CDW. Image parameters: $V_b = 260 \text{ mV}$, $I_t = 300 \text{ pA}$. b) Corresponding FFT plot of the image presented in panel a). Each color labels a different periodicity: purple (atomic), green (1T-CDW) and blue (1H-CDW). c) dI/dV spectrum performed on the same 1H area with the same tip used to perform the image shown in panel a). The hump observed at 500 mV is produced by the upper edge of the lowest 1H conduction band. The feature measured at +260 mV is related with the Upper Hubbard band from the 1T layer underneath. STS parameters: $V_b = 1 \text{ V}$, $I_t = 700 \text{ pA}$, $V_{mod} = 4 \text{ mV}$. d) Plot of the absolute intensity of the 1st order FFT spots for each periodicity as a function of the sample bias voltage.

Development of tungsten carbide nanowire superconducting detectors by pulsed focused ion beam induced deposition (PFIBID)

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Superconducting nanowire single-photon detectors (SNSPDs) fabricated via Pulsed Focused Ion Beam Induced Deposition (PFIBID) using tungsten hexacarbonyl $[W(CO)_6]$ precursor remain largely unexplored [1-3]. In this study, we present a method for fabricating tungsten carbide (WC) nanowires on SiO_x/Si substrates with pre-patterned gold electrodes using PFIBID. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) characterization show that the resulting nanowires exhibit high aspect ratios with dimensions of approximately 200 nm in width, 50 nm in thickness, and 10 μm in length.

Superconducting transition measurements were performed in a closed-cycle helium cryostat with a base temperature of 3.8 K, revealing a critical temperature (T_c) of 4.92 K and a critical current of 10.44 μA at 3.8 K. Under low-intensity pulsed light illumination ($\lambda = 640$ nm, 1 MHz), we observe a fast electrical response (rise time \sim 2.2 ns) and low decay times (\sim 4.6 ns). Photoresponse mapping reveals the spatial distribution of the electrical response, demonstrating a latching behavior with spatial resolution exceeding the Rayleigh criterion limit.

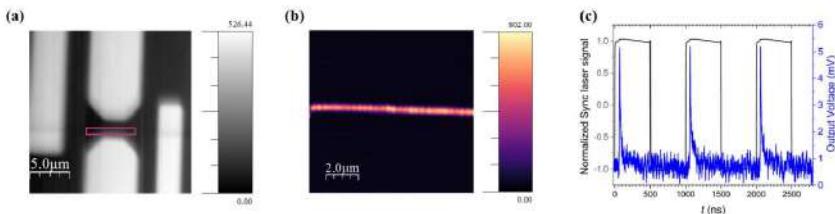


Figure 1. (a) Reflectance image of the device. Scale bar units are in μV . (b) Electrical response map of a $10 \mu m \times 10 \mu m$ region of the nanowire (obtained from inset region in (a)) under 7 nW laser illumination ($\lambda=640$ nm, 1 MHz) and $Ibias = 9.84 \mu m$. The lateral scale bar units are in millivolts. (c) Single-shot oscilloscope trace of a typical output pulse at 10.4 μA bias current amplified with a 50-dB gain and averaged 5000 times (blue curve). Sync pulsed laser signal at 1 MHz (black curve).

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Tip Enhanced Photoluminescence of individual molecules

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The increasing interest in probing the local optical properties of individual quantum emitters, such as single molecules and quantum dots, has positioned Tip-Enhanced Photoluminescence (TEPL) and Tip-Enhanced Raman Spectroscopy (TERS) as essential techniques, owing to their capability for spatial resolution at the atomic scale. Precise control over tunneling nanocavities of scanning tunneling microscopes (STM) with sub-nanometer accuracy enables spatial mapping of the TEPL and TERS spectra for individual molecules, achieved by focusing a laser into a nano junction that confines the electromagnetic field within increasing the emitted signal intensity¹. In this study, we present TEPL and TERS spectra for FeCITPP molecules within an STM junction formed by a silver tip and an Ag(111) substrate, illuminated by a 633nm laser. The complex evolution of TEPL and TERS spectra in response to varying tunneling parameters, alongside the necessity of tuning the plasmonic response of the nanocavity to the fluorophore emission, underscores the critical role of tunnel junction geometry in determining emission efficiency.

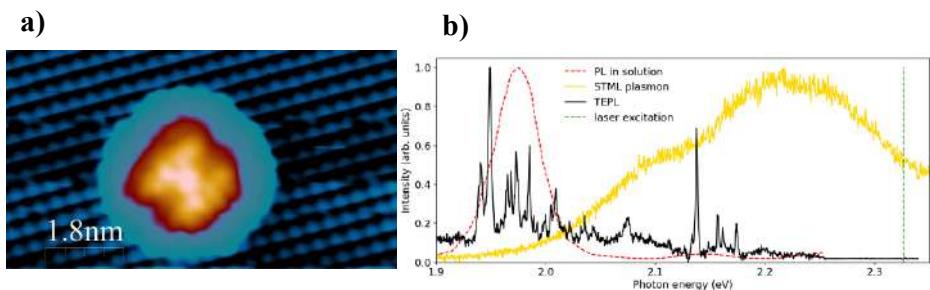


Figure 1. **a)** STM image of a single FeCITPP molecule deposited over NaCl decoupling bilayer on top of Ag(111) surface. $I_{sp} = 2\text{pA}$ $V_b = 1.9\text{V}$. **b)** Black curve: TEPL spectra of FeCITPP single molecule $I_{sp} = 20\text{pA}$ $V_b = 0.5\text{V}$. Red curve: Photoluminescence spectra of FeCITPP molecules in solution². Yellow curve: Plasmonic response of the STM nanocavity. $I_{sp} = 500\text{pA}$ $V_b = 2.7\text{V}$. Green curve: 532nm laser

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Volatile and non-volatile resistive switching in three-terminal memtransistor based on mechanically exfoliated MoS₂

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Mariela Menghini^b and Daniel Granados^a

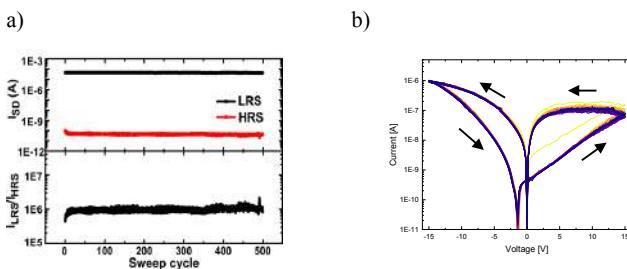
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Memristive-like behaviour has been widely demonstrated in 2-terminal MIM-based (Metal-Insulator-Metal) systems. Two-dimensional materials have become core active materials for novel electronic, optoelectronic and sensing applications. Transition metal dichalcogenides (TMDs) and other low-dimensional materials, such as hexagonal boron nitride (hBN), exhibit memristive behaviour [1]. This makes them attractive candidates as building blocks for resistive memories and neuromorphic computing devices [2].

Here, we study the memristive behaviour on 3-terminal devices based on few layer MoS₂ [3]. The devices can exhibit volatile and non-volatile resistive switching. A gate voltage is used as an extra knob to modulate the resistance switching window. We investigate the influence of contact pad geometry and symmetry in the characteristic IV curves and the relationship between optical and memristive properties.

The devices were fabricated by a mechanical exfoliation process, from natural bulk MoS₂, using the scotch tape method and transferring few-layer MoS₂ flakes onto a Si commercial substrate with a 290 nm thick SiO₂ layer on top. The memristive-like behaviour has been studied in freshly exfoliated devices at room temperature and low temperatures, under atmospheric and high vacuum conditions. A gate voltage (V_G) pulse can be used to modulate the resistance change window, i.e. the ratio I_{LRS}/I_{HRS} (where I_{LRS} and I_{HRS} are the currents in the low and high resistance states, correspondingly), by few orders of magnitude. The influence of pad geometry and symmetry in the memristive behaviour was studied by using the electrodes defined by electron-beam lithography with varying contact length (L) between 1.7 μ m and 3.2 μ m and contact width (W) between 1 μ m and 3 μ m.

Temperature dependent IV characteristics were used to determine the transport mechanisms and the Schottky barrier height in our devices.



a) Endurance of high (HRS) and low (LRS) resistance states (top) and I_{LRS}/I_{HRS} at $V_D = 7.5$ V (bottom).
b) Characteristic curve of a non-volatile device (sweeps 1-50).

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Excitonic insulating states in doped WTe₂ monolayers

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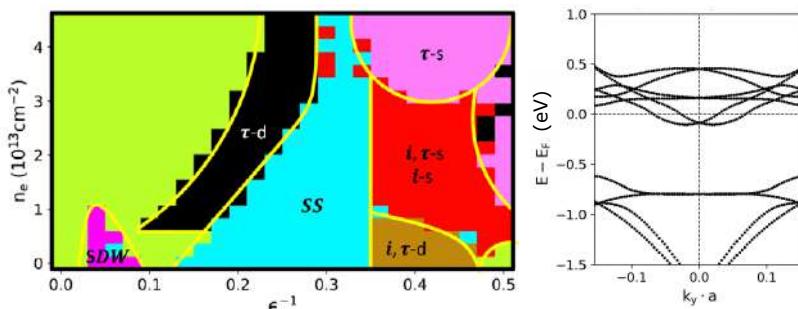
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Due to the Coulomb interaction strength, a bandgap can be opened in the band structure of a material due to the condensation of electron-hole pairs, that is, an excitonic condensate [1]. Even though it had been proposed in the past, it has not been until the recent years that experimental evidence may support the existence of this state in transition metal dichalcogenides monolayers [2]. In particular, monolayer 1T' WTe₂ has shown a plethora of promising correlated quantum states, from quantum spin hall insulating to unconventional superconducting phases [3]. Without interactions, monolayer 1T' WTe₂ is semimetallic, therefore electron and hole Coulomb instabilities could drive the pairing mechanism for the observed experimental behaviors. Moreover, a repulsive on-site interaction mechanism has been proposed theoretically as the origin of unconventional superconductivity that appears at low-density electron doping [4].

In this work, we employ a Hartree-Fock approach to characterize the excitonic states that arise in the system and we construct the correlated phase diagram of this material. We find a zoo of broken symmetry phases and two different excitonic states and analyze their particular spin ordering. Interestingly, each state features a different spin order, one with a spin density wave (SDW) and the other with a spin spiral (SS) state. This SS is compatible with the lack of charge modulation observed in the experimental data.



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Studying quantum transport in molecules: conductance and thermopower.

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In this presentation, I will describe our efforts towards the measurement of conductance (G) and thermopower (S) in various single-molecule junctions. In particular, I will highlight several families such as aromatic/antiaromatic conjugated compounds and porphyrin nanoribbons. Molecular electronics is the field that studies the use of molecules as building blocks for electronic devices by using their ability to self-assemble, their atomic precision and their quantum effects. For studying the properties of quantum transport in molecules different techniques have been developed. Among the different charge transport phenomena that have been demonstrated, the Seebeck effect is of particular interest. This is the appearance of a potential difference across a junction due to a temperature gradient, both related through the Seebeck coefficient, $S = -\Delta V / \Delta T$.

The Seebeck effect in molecular junctions paves the way to the development of cheap, environmentally friendly and high efficiency molecular thermoelectric devices, besides giving us insight to electronic transport details. The sign of S is dependent on the position of the Fermi level with respect to the HOMO and LUMO states of the molecules under study, something which is difficult to access using other routes. From a practical point of view, numerous efforts are been devoted to study ways to increase its absolute magnitude through the smart design of the core of molecules, as it is of the upmost importance to increase both the Figure of Merit ZT and the Power Factor GS^2 of thermoelectric devices, which determine its efficiency and applicability.

In order to study this phenomenon, we use the Single Molecule Break Junction (SMBJ) technique using an STM. It consist on the collision of two metal electrodes in the presence of the molecule under study, which, by further retracting said electrodes, might be trapped between them, forming what is known by molecular junction. In this work, my aim is to explain the techniques we are currently using to explore both conductance and Seebeck coefficient through families of aromatic and antiaromatic compounds (whose reduced bandgaps are expected to be related to high values of S). Besides, I also intend to explain the new techniques we are developing to explore the thermopower of porphyrin nanoribbons. Porphyrins have inherently small HOMO-LUMO gaps, moreover they are highly stable, which allow us to charge the molecules *in situ*, giving access to different oxidation states. The implications of charged molecules upon the Seebeck coefficient will be discussed.

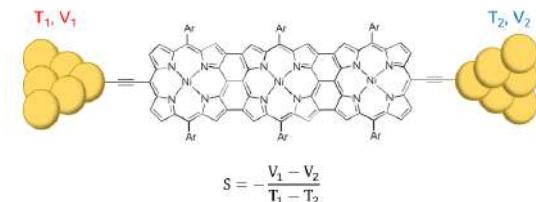


Figure: molecular junction formed by a porphyrin trimer between two metallic electrodes. By Seebeck effect, we can generate a measurable voltage difference in the molecule imposing a different temperature to each electrode,

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On-surface Synthesis of π -magnetic Au-coordinated Porphyrins

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π -magnetic compounds on surfaces have emerged as a powerful platform to interrogate spin interactions at the atomic scale, with great potential interest in spintronics and quantum technologies. Magnetic interactions through covalent bonding in carbon-based atomically precise structures have been systematically studied in the past years. However, the capabilities of coordination chemistry in terms of spin exchange interactions have yet not been illustrated. To tackle this challenge, here we take advantage of an ex-professo synthesized porphyrin precursor equipped with carbonitrile functional moieties. Our scanning probe microscopy studies reveal that the deposition of the precursor on a hot Au(111) substrate affords the formation of two distinct reaction polymers, the majority one being π -extended porphyrin units, coordinated by two-fold CN-Au-CN interactions and the minority one being porphyrin dimeric tapes, also gold coordinated. Either scanning by perturbative conditions or by tip-induced pulses, two hydrogens, coming from previous concomitant passivation, could be removed per monomer forming coordinative wires based on open-shell monomers featuring a S=0 ground state [1]. Furthermore, monomers do not get altered by nearest neighbors, behaving as unique magnetic entities. Altogether, our study reveals the capabilities of on-surface covalent synthesis and coordination chemistry to form unprecedented open-shell low-dimensional coordination polymers, while preventing the interaction between spins of the constituent monomers.

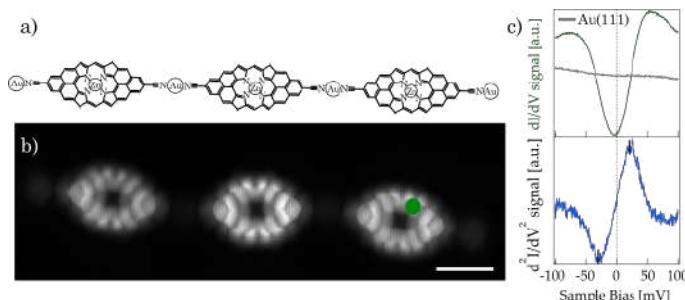


FIGURE 1. A three-membered porphyrin chain. a) Chemical scheme of the fully polymer. b) STM image at constant height. Scanning parameters: 20 mV. Scale bar = 1 nm. c) dI/dV and d^2I/dV^2 spectroscopy on a monomer within polymer at the position indicated by the green dot in b).

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Heat transport across nanometre-sized gaps

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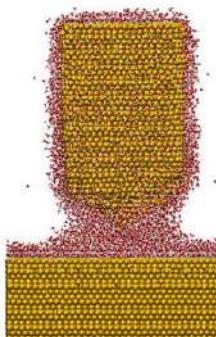
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Heat transfer in nanoscale gaps is of key relevance for a variety of technologies. Recent experiments [1,2] have reported contradictory results shedding doubts about the fundamental mechanisms for heat exchange when bodies are separated by nanometre-sized gaps. Here, we aim at resolving this controversy by measuring the thermal conductance of gold atomic-sized contacts with a custom-designed scanning tunnelling microscope that incorporates a novel thermal probe. This technique enables the measurement of the thermal and electrical conductance in different transport regimes. When the electrodes are separated by a nanometre-sized gap, we observe thermal signals whose magnitude and gap size dependence cannot be explained with standard heat transfer mechanisms. With the help of non-equilibrium molecular dynamic simulations, we elucidate that these anomalous signals are due to the thermal conduction through water menisci that form between tip and sample under customary operation conditions. Our work resolves this fundamental puzzle and suggests avenues for the investigation of heat conduction in atomic and molecular junctions.



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Designing organolanthanide sandwich complexes by on-surface synthesis

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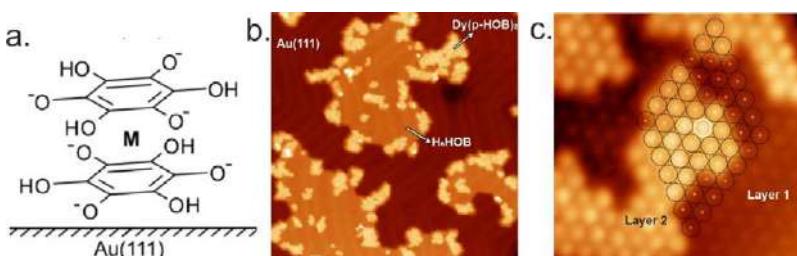
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Organometallic compounds are structures made up of metal atoms and organic molecules with at least one chemical bond between a carbon and metal atom. Surface chemistry permits their synthesis and local studies down to the single molecule level. However, when these complexes are adsorbed on metallic surfaces, hybridization of orbitals due to the proximity of the metal atoms to the substrate and charge transfer can change their properties [1], reducing the magnetic moments [2] and inducing interface states [3]. A possible strategy to overcome this problem is to isolate the metal atoms by sandwiching them in between the organic complexes. Lanthanide-based organometallic sandwich compounds exhibit high blocking temperatures, remanence, high anisotropy, and slow relaxation times [4] and are highly intriguing as a potential for single molecule magnetism with possible applications in nanomagnetism, data storage, spin-based devices, among many other applications [5].



a) Graphical representation of the organometallic sandwich complex (M represents Dy or Er atom). b) STM image: size 60nm², overview of partially grow Dy(p-HOB). c) A superimposed model (black circles) centered in a second layer molecule (white circle) shows that the second layer molecules are perfectly aligned with the first layer molecules.

In this work [6], we report the design of two new organolanthanide mononuclear sandwich complexes adsorbed on a Au (111) surface. We have studied their structural, electronic, and chemical properties using scanning tunnelling microscopy and spectroscopy and X-ray photoelectron spectroscopy. Our results show that the presented compounds are composed of partially deprotonated hexahydroxybenzene molecules sandwiching Dy or Er atoms with +3 oxidation state. The X-ray absorption spectroscopy and circular magnetic dichroism measurements reveal that the erbium-based species is magnetically isotropic, while the dysprosium-based compound has an in-plane magnetism, despite displaying similar self-assembly, showing the role of lanthanide atoms in tuning the magnetic properties. To the best of our knowledge, we present the first report of the synthesis of organometallic sandwich complexes by a bottom-up approach on a catalytic metallic surface.

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Time Resolved Magneto Optic Kerr Effect Setup At IMDEA Nanoscience

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We have built a Time Resolved Magneto Optic Kerr Effect (TR-MOKE) setup for studying ultrafast demagnetization. TR-MOKE is the powerful pump probe technique capable of measuring magnetization dynamics in materials having the magnetic order with femtosecond time resolution via changes the probe polarization¹. In our system the pump and probe pulses are 800 nm and 400 nm, respectively, with approximately 50 fs temporal resolution. As a first experiment we have pumped thin film ferromagnetic material PtCo at different fluences. Recent research shows simulations which claim that there is possibility creating Skyrmions using ultrafast lasers². Our next goal is to nucleate the Skyrmions using this pump probe technique and then we will see how their formation manifests in the magnetization dynamics at very short time scales.

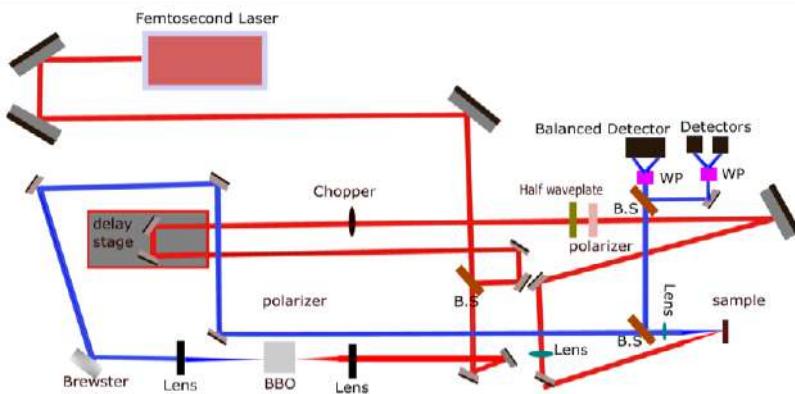


Figure 1: Schematic of the TR-MOKE setup at IMDEA Nanoscience.

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Ultrafast hole dynamics in Colloidal Quantum Dots revealed by Ultrafast X-ray Spectroscopy

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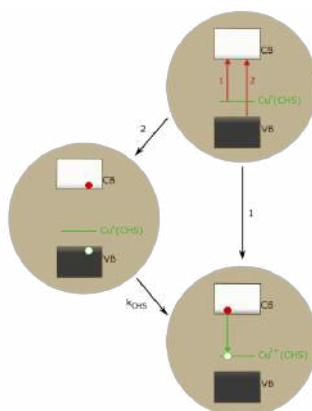
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Semiconductor CuInS₂ (CIS) quantum dots (QDs) exhibit low toxicity, excellent charge-transport properties, and remarkable photoluminescence features. These attributes make CIS QDs highly promising for optoelectronic applications, such as highly efficient solar cells, luminescent solar concentrators and deep-tissue bioimaging¹. To develop our fundamental understanding of nanoscale photophysics and to optimize the design of devices, several mechanisms of recombination in CIS QDs have been proposed, modelling the population dynamics of correlated electron-hole pairs (bound excitons). While most suggest that radiative recombination results from the interaction between an electron in the conduction band and a hole in the so-called confined hole state (CHS)²⁻³, no research has provided direct experimental evidence for the existence of this intra-gap state. The existence of such a state, arising from a defect of Cu⁺ that can get oxidized to Cu²⁺ by the hole, would explain the large Stokes shift and broad photoluminescence exhibited by the CIS QDs and has been theoretically predicted and postulated for a long time.



In this work, we aim to understand and confirm the possibility of observing the formation process of the CHS and the localization of a hole in the CHS. We approached these questions through a combination of ultrafast optical and X-ray laser (XFEL) pump-probe techniques on Zn-doped core-shell CIS QDs of different composition. The element and oxidation state specificity of X-ray spectroscopies, both X-ray absorption (XAS) and X-ray emission (XES) spectroscopy, will serve as a direct probe to track recombination and localization dynamics of photogenerated holes, while optical probes will follow the electron dynamics. We probed the oxidation state of Cu fs-resolved K-edge XAS at two different light sources; PAL-XFEL in South Korea and LCLS in the USA, while we used non-resonant XES at the European XFEL. This extended study allowed us to gain insights and correlate the observed charge carrier dynamics, influenced by the laser fluence, with the underlying CIS QD structures, the degree of their surface passivation and the different Zn doping levels. This is then complemented by our time-resolved optical studies monitoring transient absorption and photoluminescence.

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Phonon Dispersion in Hexagonal Boron Nitride: A Continuum Model Approach

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The twisted stacking of layers in van der Waals materials, forming moiré superlattices, has opened up new avenues for exploring the physics of strongly correlated systems and various emergent phenomena. Among these materials, hexagonal boron nitride (hBN), though less well-known than its isostructural counterpart graphene, stands out due to its insulating nature, oxidation resistance, high thermal conductivity, and exceptional mechanical strength. These properties, coupled with the potential to engineer new behaviors through twisted bilayer configurations, position hBN as a versatile material for state-of-the-art applications.

One of the primary challenges in harnessing these applications lies in understanding phonons (propagating atomic vibrational waves), which critically influence a material's thermal, mechanical, optoelectronic, and transport characteristics. Recently, Cappelluti et al. [1] developed a continuum model to describe the lattice dynamics of twisted bilayer graphene, revealing significant band flattening across nearly all high-frequency in-plane lattice vibration modes, including the valley Dirac phonon, valley optical phonon, and central-zone optical phonon bands. This discovery provided new insights into phonon scattering in complex two-dimensional materials.

Building on these findings, our primary objective was to extend this continuum model to other two-dimensional materials, with a particular focus on hBN. In this study, we applied Density Functional Perturbation Theory (DFPT) using the Quantum ESPRESSO package with Perdew–Burke–Ernzerhof (PBE) functionals within the Generalized Gradient Approximation (GGA) and PAW pseudopotentials. This approach allowed us to optimize the structure and obtain phonon dispersion bands for both monolayer hBN and various stacking configurations [2].

As a result, our simulations confirmed the validity of the continuum model for capturing phonon dispersion. Specifically, the continuum model accurately captured the behavior of phonon dispersion at high-symmetry points in the Brillouin zone, including the LO/TO splitting observed in bilayer configurations. This robust representation allowed us to perform a deeper analysis of the phonon dispersion in twisted bilayer hBN, offering valuable insights into its potential for novel and innovative applications.

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Structural and Functional Analysis of Human Papillomavirus (HPV) Protein: Insights into Physicochemical Properties, Interaction Networks, and Therapeutic Targeting

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Human papillomavirus (HPV) is a leading viral infection responsible for numerous new cancer cases globally each year, including cervical cancer and other types. Over millions of years, HPVs have evolved to replicate within various animal species, including humans. Viruses that have co-evolved in this gradual manner typically establish persistent asymptomatic infections, characterized by the production of virions without causing noticeable illness. This study focuses on analyzing the HPV protein sequence and conducting structure-based functional evaluations. It gathers data on physicochemical properties, domain predictions for functional forecasting, and protein-protein interaction (PPI) networks, along with predicting and analyzing both 2D and 3D structures. The physicochemical analysis revealed that the protein sequence contains more negatively charged residues than positively charged ones. The Grand Average of Hydropathy (GRAVY) value indicates that the protein exhibits hydrophilic properties. Additionally, the analysis identified a polyadenylate-binding protein within the sequence, which binds to the poly(A) tail of mRNA and serves as a post-transcriptional regulator. Gene ontology analysis highlighted the protein's involvement in cellular, molecular, and biological processes. Through the PPI network, interactions between this protein and ten other proteins were identified. Secondary structure evaluation showed that random coils constitute the predominant structural element, followed by alpha helices and extended strands. Furthermore, the 3D structure of the protein was reconstructed using three advanced modeling tools: AlphaFold, I-TASSER, and SWISS-MODEL. Among these, SWISS-MODEL provided the most accurate 3D structural prediction. Given the functional role of this protein, it is critical to suppress its activity using potential drugs or vaccines to prevent further infection spread.

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Magneto-transport and anomalous Hall effect in ferromagnet/superconductor heterostructures

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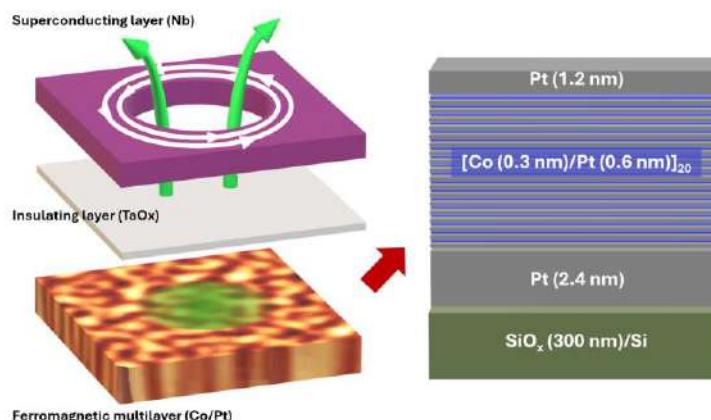
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Ferromagnetism and superconductivity attract a lot of attention in the condensed matter physics community not only due to the rich physical phenomena they embrace but also due to their great potential in different applications (memories, sensors, quantum devices...). Although they are considered antagonist effects, the interplay between them can lead to a wide variety of exotic phenomena. Some examples are superconducting vortex pinning induced by magnetic nanostructures [1], domain wall superconductivity [2], triplet superconductivity [3] and superconducting vortex – magnetic skyrmions interactions [4,5].

In this work, we investigate magneto-transport properties of a ferromagnetic (FM) multilayer with perpendicular magnetic anisotropy (PMA) in contact with a superconductor (SC). The SC is either a plain or nanostructured Nb film or an exfoliated flake of NbSe₂. We observe clear changes in the magneto-resistance and Hall resistance of the FM at temperatures below the transition temperature of the SC. The symmetry of the Hall response indicates that these changes are likely not due to topological effects but possibly caused by modifications in FM multilayer domains or due to proximity effects.



Ferromagnetic/Superconductor hybrid system [5]

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Integration of Functionalized Carbon Nanomaterials in Spiro-OMeTAD for Enhanced Performance of Perovskite Solar Cells

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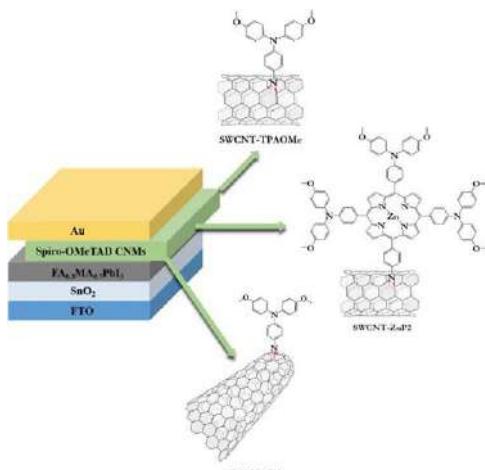
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The rising demand for clean energy has led to an increased interest in sustainable energy sources, particularly photovoltaic (PV) technology. Significant efforts have been made to improve PV technologies that directly convert sunlight into electricity in an environmentally friendly way. Among various light-harvesting materials, perovskite solar cells (PSCs) have gained substantial recognition worldwide for their ease of fabrication and low production costs.¹ PSCs typically have a cubic structure, represented by the formula ABX_3 , and are built with a sandwich-like design that includes a light-absorbing hybrid halide perovskite layer between a semiconducting oxide (ETL) and an organic hole-transporting material (HTM). Among these HTMs, Spiro-OMeTAD has been extensively studied for its role in enhancing PV performance.²

In this study, we synthesized new functionalized carbon nanomaterials (CNMs) named SWCNT-TPAOme, SWCNT-ZnP₂, and CNH-TPAOme, and integrated them into doped Spiro-OMeTAD. This integration improves charge extraction, optimizes the surface morphology and interface between Spiro-OMeTAD and the perovskite layer, and enhances energy level alignment with the perovskite material.³

PSCs fabricated using these functionalized CNMs achieved significant improvements in efficiency, short-circuit current density (J_{sc}), fill factor (FF), and open-circuit voltage (V_{oc}). The device incorporating SWCNT-ZnP₂ achieved a power conversion efficiency (PCE) of 19.65%, while devices using SWCNT-TPAOme, CNH-TPAOme, and conventional Spiro-OMeTAD (without CNMs) reached PCEs of 18.85%, 17.90%, and 18.01%, respectively. This study demonstrates that the incorporation of functionalized CNMs into Spiro-OMeTAD can significantly enhance both the performance and stability of PSC devices.



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TADF-Protein Biohybrids: Santa's Secret to Efficient Light Harvesting Systems

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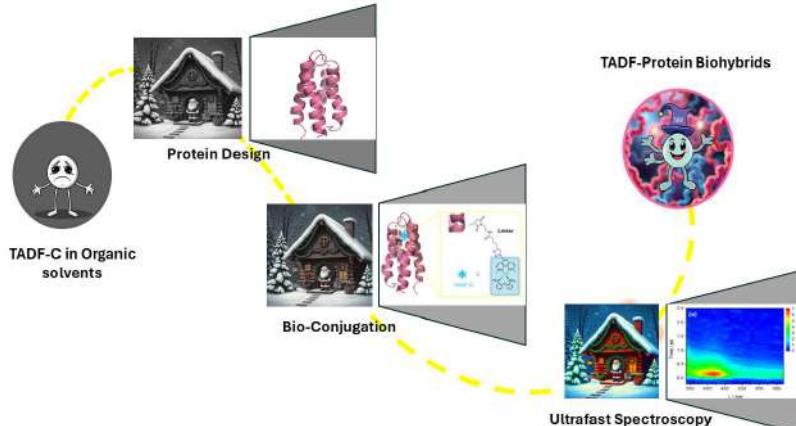
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Thermally Activated Delayed Fluorescent chromophores (TADF-Cs) possess phenomenal photophysical properties like prolonged photoluminescence life-time and high quantum yield alluring their applications in light emitting diodes and photocatalysis etc.^[1] Yet, these, most prevalently large organic molecules face limitations viz., achieving efficiency roll-off, color purity, suitable host materials and water solubility.^[2] Herein, we advocate a novel approach to augment TADF properties enabled by a protein cavity providing conformationally rigid environment; enabling nuanced control of the energy gap between singlet excited state and triplet state. In the present study, we shall first twelve into structural design of protein^[3] (α -proteins) tailored for labeling and enhancing photophysical properties. While taking care of the solubility of TADF-Cs in aqueous environment, protein confers additional dimension to introduce amino acids of interest by site-specific mutagenesis (SSM); for instance, creating localized electric fields (charged amino acids) and incorporation of thiol groups. Albeit it, SSM enables to buttress the photophysical properties of TADF-C intact, resulting from undesired electron transfer process in the excited states.^[4]

We shall employ the two distinct bio-orthogonal methods^[5] for incorporating TADF-C into the protein pocket. By using a medley of Cu Catalysed Click chemistry (dye functionalization with linker: alkyne maleimide) and subsequent Micheal reaction (cysteine-maleimide) facilitating the site-specific labeling; termed as "linker-method". We envisage to introduce unnatural amino acid (having strained cyclo-alkyne) translationally and then with Cu-free click chemistry; termed as "UAA method". In much a broader perspective, by using two model proteins (α -4 protein and α -3 proteins), we shall explore the role of cavity space accessible to the TADF-C in the pocket and rationally underscore how this influence photophysical properties of the chromophore. Our initial results show the successful functionalization of linker to the TADF-C precursor. In a nutshell, by using a combination of protein designing, bio-orthogonal chemistry and ultrafast spectroscopy; the proposed project can thus unravel the relatively less explored photophysical properties of TADF-Cs in a biomolecule environment, with potential for commercial applications.



‡ Schematic of TADF-biohybrids. Starting from protein design, to site-specific labeling and subsequent characterization by time-resolved ultrafast spectroscopy.

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High Q Spontaneous Emission and Ultra-Low Lasing Threshold in Polymeric Microspheres

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Conjugated polymer (CP) and organic dye-based microspheres of very high definition and outstanding photonic and luminescent properties have been prepared by two different techniques. Poly[(9,9-di-*n*-octylfluorenyl-2,7-diy)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diy)] (F8BT) and mixtures of the latter with poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV), as well as PI2PhDPO have been used. Structural characterization demonstrates good sphericity and low surface roughness. Spontaneous emission for the spheres exhibits Mie resonances of high-quality factor ($Q > 1800$). Upon pumping with a pulsed Nd:YAG laser at 355 nm, we have obtained lasing at low threshold fluences ($\approx 4 \mu\text{J}/\text{cm}^2$) with instrumentally limited linewidths corresponding to $Q > 18000$. Lasing in microspheres composed of blends of both CPs, coupled by Förster resonant energy transfer (FRET), has been observed at extremely low threshold fluences down to $\approx 0.5 \mu\text{J}/\text{cm}^2$. These spherical resonators are promising candidates in the search for low-threshold organic microlasers pumped by diode lasers, which are of interest, for example, for ultrasensitive optical sensing application.

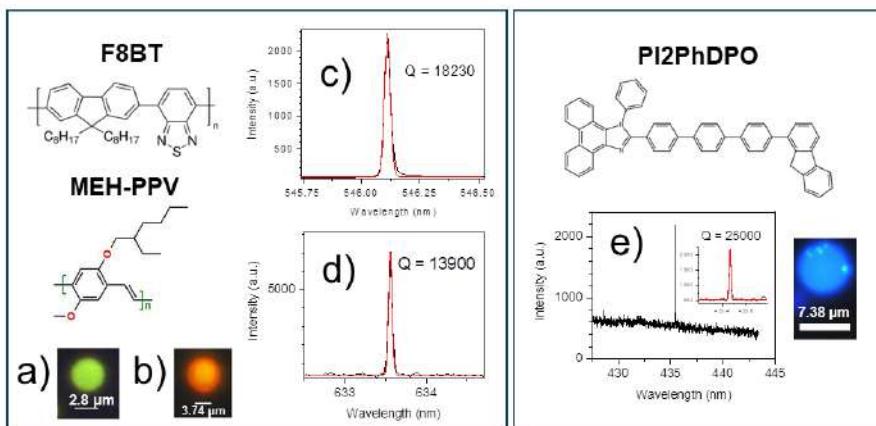


Figure 1. Microscope camera images of microspheres of a) pure F8BT and b) 5% MEH-PPV in F8BT. Laser linewidth measurements of individual microspheres of c) pure F8BT, d) 5% MEH-PPV in F8BT and e) 5% PI2PhDPO in polystyrene. All measurements are limited by the instrumental resolution. Measurements of c) and e) have been performed in second order of the spectrometer. Excitation wavelength 355 nm. Microscope camera images of the microspheres are shown.

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Can we tune artificial photosystems to perform photocatalysis?

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Engineering photostable dyes is essential for enhancing their photophysical performance and device efficiency. Strategies to enhance the dye photostability are based in dye photoprotection. Some approaches to enhance photoprotection involve changes in the molecular structure of the dye or encapsulating them on complex metal-organic frameworks (MOFs). However, there is a lack of control in synthesis and complexation efficiency. A bioinspired strategy is embedding the dyes in protein environments that directly modify the dye's photophysical properties based on amino acid-dye interactions. In particular, previous work has shown the implication of tryptophan amino acid in photoprotection of organic dyes [1]. The aim of this work is to determine the role of Tryptophan in this photoprotection processes. In particular, we use different spectroscopic techniques such as Fluorescent Spectroscopy and Ultrafast Transient Absorption Spectroscopy to study the effect of the Tryptophan in bodipy photoprotection. We show that tryptophan accelerates the bodipy's excited state decay via photoinduced electron transfer as main photoprotection mechanism. This result deepens our understanding on protein-dye interactions and consolidates proteins as a promising candidate of dynamic exciton modulators.

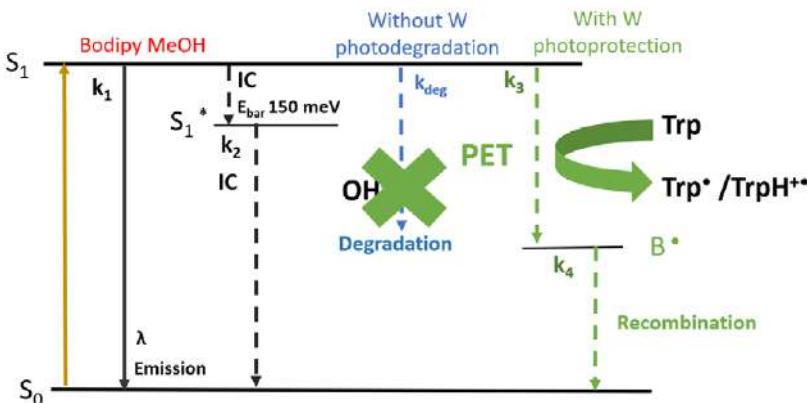


Fig. 1: Proposed mechanism of excited state dynamics in bodipy after irradiation in different media, in absence and presence of Tryptophan. Tryptophan involves in an ultra-fast photoinduced electron transfer (a-PET) with bodipy.

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Harnessing Energy and Electron Transfer Processes in Engineered Bio-Hybrids for Enantioselective Photocatalysis

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Photocatalysis has proven to be a powerful tool for rupturing and forming chemical bonds under visible light irradiation. Photoactivation of catalysts allows access to various reactive intermediates via photoinduced energy and electron transfer processes¹. On the other hand, enantioselective catalysis has been thriving as an independent research field for the selective preparation of enantiomerically pure compounds as pharmaceutical ingredients and drug molecules². Over the past decade, BODIPY (Boron-dipyrromethene) dyes have emerged as promising metal-free catalysts encompassing different tactics to achieve several photochemical transformations under visible light irradiation³. However, selectivity and asymmetric photochemical conversion in environmentally benign conditions of BODIPY-based photocatalysis remain challenging because creating the chiral center on BODIPY derivatives will give synthetic difficulty as low product yield. Furthermore, the required activation of reactive intermediates during substrate binding to the chiral center and deactivating them when no substrate is present makes this type of reactions even more challenging. Within this context, we are willing to use the protein microchiral environment, which will provide high chemo-, regio-, and stereoselectivity for enantioselective catalysis under sustainable reaction conditions. Herein, we used the Lactococcal Multidrug Resistance Regulator (LmrR) protein because of its promiscuous dimeric hydrophobic pocket that can bind planar organic molecules through multiple supramolecular interactions⁴. Previously, it has been shown that the recruiting of tetra-methyl-meso-phenyl BODIPY into LmrR_W96 protein facilitated the photoinduced electron transfer between the tryptophan unit of LmrR_W96 and BODIPY quenching its photochemistry⁴. To overcome this challenge, we synthesized the diido and dibromo substituted tetra-methyl-meso-phenyl BODIPY to favour the triplet state formation. This reactive state competes with the fast quenching electron transfer process in the case of an unsubstituted one. This approach allows us to take advantage of the protein's chiral environment and the BODIPY's photochemistry. We found the dissociation constants (K_d) for all three LmrR-[BODIPY] complexes were relatively high, confirming that the aromatic interactions between tryptophan and BODIPY unit played a major role in their binding affinity. We also characterized the thermal stability of the complexes and excited-state photophysical properties based on steady-state and ultrafast spectroscopic techniques. All these studies will help us understand the photoinduced energy or electron transfer processes of developed LmrR-[BODIPY] complexes to select the best candidate for enantioselective photoconversion. This novel strategy will have an impact on tuning the photoredox properties of LmrR-[BODIPY] complexes for generating regio- and stereoselective chiral products that could potentially be used as synthetic precursors and drugs under sustainable reaction conditions.

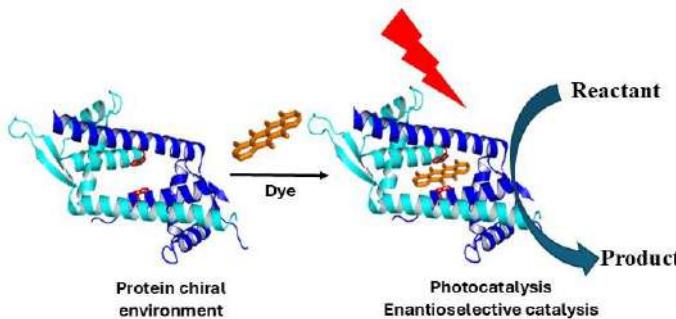


Figure 1: General Schematic for generating artificial photoenzymes for enantioselective photoconversion.

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THE RELEVANCE OF AMINO ACID -CHROMOPHORE INTERACTIONS IN PROTEIN CONFORMATIONAL CHANGES

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Natural photosystems show remarkable light harvesting efficiency due to specific interactions between chromophores and protein structures 1. Protein motions and dynamics influence geometrical constraints and the chromophore environment, affecting pigment coupling and energy transfer pathways. Understanding the nature of protein-chromophore coupling is an open question that still needs to be addressed. However, the complexity of the photosystems hinders key amino acids, adding a limit in this field. In this work, we propose a solution to study the impact of amino acid-chromophore interaction by developing easily manipulated biohybrid assemblies as model photosystems. The designed biohybrids are formed by a de novo α -helix protein and a pyrene chromophore covalently bound in the protein pocket (Figure 1A). Close to the pyrene, we located specific amino acids that trigger quadrupolar interactions through different amino acids (phenylalanine, tyrosine, valine, and tryptophan) with different electronic densities that will interact with the pyrene at various orientations and strengths (Figure 1B). We define a new parameter called bio-chrome coupling to evaluate these interactions. This parametrization allows the extraction of the real effect of the interaction in the folding state. Using spectroscopic methods, we demonstrate that different biochrome coupling alters the conformation of the biohybrid between open and closed, affecting the dynamics of excited states of the chromophore. Our parametrization strategy from interaction to the bio-chrome coupling introduces a new design strategy that will allow us to evaluate the engineered bio-hybrid in an entirely new way. We have obtained, so far, static conformational changes, but this strategy set the basis to form dynamic systems that will allow, ultimately, to show the real effect of protein motions in light harvesting. A thorough understanding of protein dynamics will allow us to use the principles used by nature to design photosystems with optimized light energy conversion for applications in photonics and photochemistry.

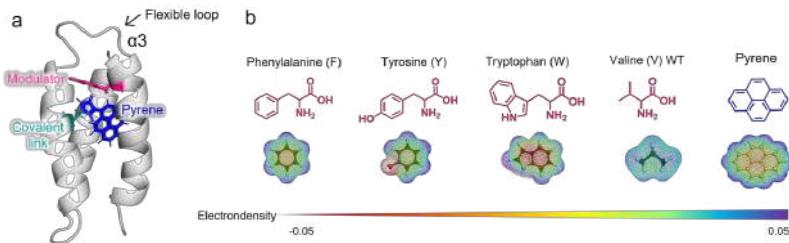


Figure 1. a. Designed bio-hybrid model with the cysteine at position 34 highlighted in green, covalently linked pyrene in blue and structure modulator at position 18 in pink. b. Selected structure modulators and pyrene with calculated electrodensity.

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Designing model photosystem for tracking protein dynamics in chromophore's light harvesting properties

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Studies in natural photosystems suggest that a correlation between protein dynamics and chromophore's excited state relaxation is key for efficient light harvesting. However, showing the impact of these protein dynamics in chromophore's light-harvesting properties is challenging due to the huge complexity of the natural systems. Artificial photosystems have emerged as a solution to perform mechanistic studies by simplifying the effects that occur in natural light-harvesting processes. However, the chromophores used in most cases have linkers that attach them to the protein structure, giving flexibility and rotational freedom to the chromophore that obscures the role of protein dynamics in the photosystem.¹ In this work, I proposed a new approach to generate the artificial photosystem based on the incorporation of the chromophore as an unnatural amino acid (UAA). We hypothesize that the direct incorporation of the chromophores into the protein backbone will allow us to track protein dynamics in real-time. To show that, we designed two photosystem models one in which the chromophore is incorporated directly into the backbone as a UAA and the other where the chromophore is attached to the backbone via a linker (Figure 1). These designs will allow us to compare whether there are significant differences in the light-harvesting properties of the chromophore depending on whether a linker is present or not. This new approach will allow the development of mechanistic studies from a completely different angle, revealing how protein dynamics affect the light-harvesting properties of chromophores.

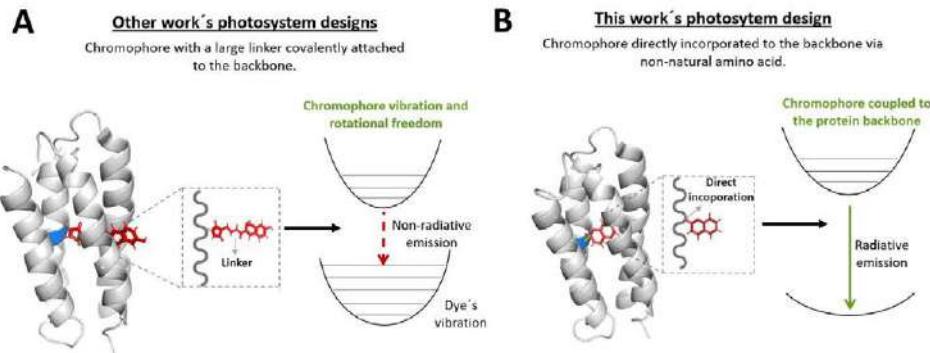


Figure 1: (a) Artificial photosystem model with an Alpha4 protein (grey) linked to coumarin-maleimide via click chemistry (red), implying weak coupling, less emission. (b) Alpha4 protein (grey) with coumarin bound as a non-natural amino acid (red), indicating strong coupling, more emission.

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Through-Bond vs. Through-Space Conjugation in Phenyl-Based Polymers

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Conjugated polymers have been used in the development of organic light-emitting diodes since the discovery of the luminescence of poly(phenylene vinylene) (PPV) in the 1990s¹. Through-bond conjugation (by the overlap of the p_z orbitals along the molecular backbone) is known to be the crucial factor in narrowing the optical gap, leading to absorbance and emission of visible light. However, recent reports on poly(phenylenemethylene) (PPM) – a polymer that, despite having local conjugation in its adjacent units, does not exhibit through-bond conjugation – presents fluorescence in the visible range². These unexpected optical properties were attributed to *homoconjugation* along the chain –that is, through-space π-orbital overlap–enabled by a near-cofacial arrangement of neighboring phenylene rings.

From experiment alone such claims are difficult to prove. Therefore, we undertook a DFT study to investigate his issue. For this we systematically compared the polymers in question, i.e. PPM, on one hand with fully conjugated polymers, i.e. PPV, and poly(phenylene) (PP) (see Figure 1). We used the oligomer approach³, an effective strategy to estimate optical properties in polymers based on those of the corresponding oligomers. To extrapolate the results to the polymer limit, the physically founded Kuhn fit was used^{3,4}. Optical excitations of the oligomers were estimated through single point calculation of vertical energy E_{vert}. While standard hybrid functionals like B3LYP are known to systematically underestimate E_{vert}, CAM-B3LYP was shown to provide a reasonable estimation^{5,6}. To assess the reliability of the methodology, we compared the results with available experimental data for PPV and PP, which showed good agreement (Figure 1.) .

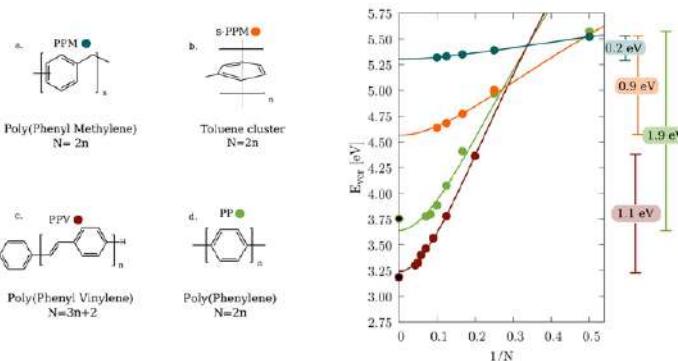


Figure 1. Extrapolation to the polymer limit for all four oligomers under study. The solid lines correspond to the Kuhn fit, the vertical lines at the right side of the graph represent the difference in E_{vert} from the monomer to the value at the polymer limit. The black dots on the y-axis show the experimental values for PP (green) and PPV (red).

The methodology was then applied to the cofacial arrangement of the toluene cluster, where the through-space overlap of the frontier MOs was maximized in order to establish an upper limit for the potential effect of *homoconjugation*. For PPM, the narrowing of the optical bandgap from the monomer to the polymer was only about 0.2 eV, being one order of magnitude smaller than the value suggested in Ref. 2. As further seen in Figure 1, the change in Evert at the polymer limit remained in the UV. This allowed us to conclude that *homoconjugation* can not compete with a through-bond conjugated system. Our study thus highlights the power of computational methods to verify or refute unproven hypotheses *in silico*, and to redirect research efforts to a common-sense physical basis.

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Photophysical Characterization of a Thermally Activated Conical Intersections in a Ni(II) Porphyrin-Nanographene Conjugate

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fs-TAS temperature-dependent measurements have been performed to study a nanographene-Ni(II) porphyrin conjugate called NP (Figure 1a). At room temperature vibrational cooling takes place in 1.6 ps, after this a small fraction of relaxed singlets decay via fluorescence emission to the ground state, this emissive recombination is quenched by an efficient intersystem crossing (ISC) to a metal centered triplets family ($T(d,d)$), which relax to the lowest triplet ($T_1(d,d)$) in 18 ps. From this, a relaxation to the ground state (S_0) takes place in only 40 picoseconds (Figure 1b,c), which is extremely fast, as $T_1(d,d) \rightarrow S_0$ involves a quantum forbidden transition that typically involves lifetimes in the order of nanoseconds. Global fit analysis is employed to modelize the mechanisms governing this fast triplet relaxation pathway. By deploying low temperature measurements, evidences for a competition between two terminal relaxation pathways from the lowest triplet to the ground state are provided. The possible relaxation pathways are: i) a $T_1(d,d) \rightarrow GS$ relaxation proceeding in timescales beyond 1.5 ns and ii) an ultrafast deexcitation triggered by a sloped conical intersection, which is thermally accessible at room temperature from the $T_1(d,d)$. The overall triplet decay at a certain temperature is linked by these two contributions. This becomes significant to identify and understand the underlying fast relaxation processes in Ni-based molecules and related transition metal complexes, paving the way for potential applications for energy harvesting and optoelectronics. [1]

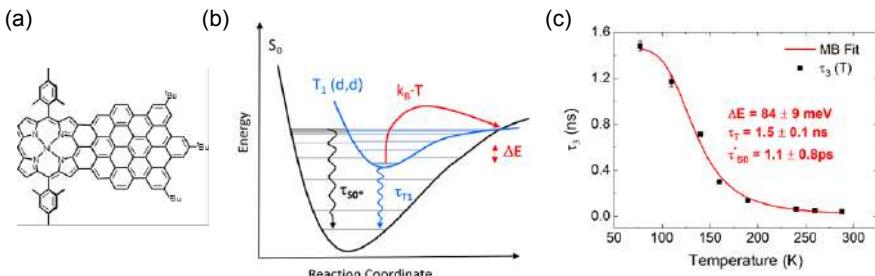


Figure 1. (a) Chemical structure of NP molecule. (b) Scheme of the potential energy surfaces involved in the deexcitation process on NP. (c) Value of the final relaxation lifetime as a function of temperature obtained by global fit analysis.

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2D material for solar-powered photocatalytic hydrogen production

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Among the candidate materials for photocatalysts to perform water splitting, a standout choice are 2D materials (with one of their dimensions in the nanometric scale), due to their high relative surface to volume ratio, higher mobilities and tunable bandgaps. Transition Metal Dichalcogenides (TMD) are a family of 2D materials with promising properties in photocatalysis. Here we propose, for the first time to our knowledge, the generation of a protein/2D-nanosheet bio-hybrid system with the objective of enhancing the photocatalytic properties of TMD 2D materials.

The functionalization of the TMD nanosheets with a protein-chromophore complex is expected to perform an expansion of the absorption wavelength range of the system thanks to the contribution from the chromophore, and improve charge carrier separation within the system, as well as an anti-aggregant function for the nanosheets.

The combination of the TMD nanosheets and the protein-chromophore complex has shown novel features in the absorption spectrum – not present in any of the components' spectra – which merit further study through different techniques to analyze dynamic behavior of the system in the femtosecond range.

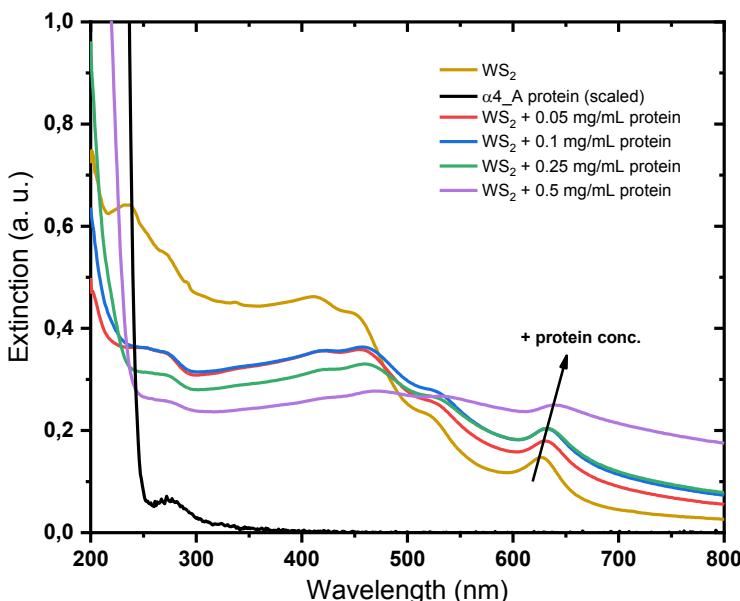


FIGURE 1. Extinction spectra for PBS-based dispersions of 2D WS₂ nanosheets alone, α4_A protein alone, and the same concentration of 2D WS₂ combined with 4 different concentrations of α4_A protein (200-800nm).

Low-threshold deep blue organic distributed feedback laser based on nanoimprinting lithography

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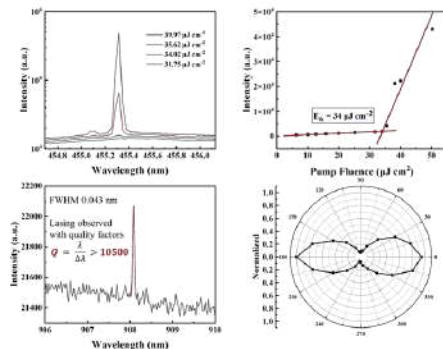
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Novel highly luminescent PI2PhDPO conjugated molecules blended with 1,3-Bis(N-carbazolyl)benzene were studied as optical gain medium in distributed feedback lasers (DFB). DFBs fabrication involved first the deposition by spin-coating of blends on top of glass substrates coated with an adhesion promoter. Subsequently, nanoimprinting was performed directly on this gain medium film. For this purpose, H-PDMS molds with periodical patterns coated with a fluorosilane monolayer were used for nanoimprinting to further improve anti-stick properties. Combined control of the nanoimprint temperature and pressure enabled to finally obtain uniform and continuous high-quality DFB gratings and achieved low-threshold, ultra-narrow linewidth (≈ 0.043 nm) with perpendicular single-mode lasing emission in deep blue wavelengths.

FIGURE



Single lasing mode with high Q factor DFB grating (top left) and variation of the output laser Intensity as a function of pump fluence (top right). Expanded views of the second order lasing modes (lower left) and linear polarized emission output (lower right). The pump polarization was fixed along the DFB lines, whereas the output intensity was filtered with a polarizer at different angles.

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Integration of Functionalized Carbon Nanomaterials in Spiro-OMeTAD for Enhanced Performance of Perovskite Solar Cells

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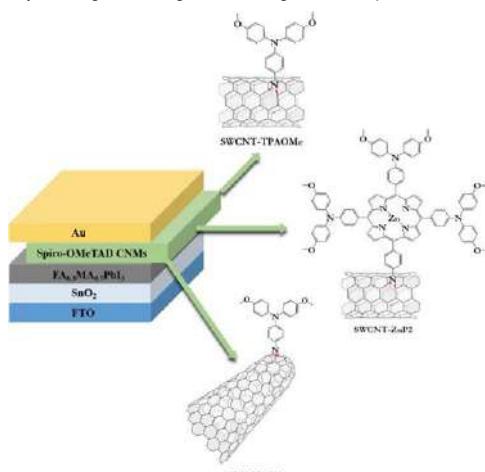
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The rising demand for clean energy has led to an increased interest in sustainable energy sources, particularly photovoltaic (PV) technology. Significant efforts have been made to improve PV technologies that directly convert sunlight into electricity in an environmentally friendly way. Among various light-harvesting materials, perovskite solar cells (PSCs) have gained substantial recognition worldwide for their ease of fabrication and low production costs.¹ PSCs typically have a cubic structure, represented by the formula ABX_3 , and are built with a sandwich-like design that includes a light-absorbing hybrid halide perovskite layer between a semiconducting oxide (ETL) and an organic hole-transporting material (HTM). Among these HTMs, Spiro-OMeTAD has been extensively studied for its role in enhancing PV performance.²

In this study, we synthesized new functionalized carbon nanomaterials (CNMs) named SWCNT-TPAOme, SWCNT-ZnP₂, and CNH-TPAOme, and integrated them into doped Spiro-OMeTAD. This integration improves charge extraction, optimizes the surface morphology and interface between Spiro-OMeTAD and the perovskite layer, and enhances energy level alignment with the perovskite material.³

PSCs fabricated using these functionalized CNMs achieved significant improvements in efficiency, short-circuit current density (J_{sc}), fill factor (FF), and open-circuit voltage (V_{oc}). The device incorporating SWCNT-ZnP₂ achieved a power conversion efficiency (PCE) of 19.65%, while devices using SWCNT-TPAOme, CNH-TPAOme, and conventional Spiro-OMeTAD (without CNMs) reached PCEs of 18.85%, 17.90%, and 18.01%, respectively. This study demonstrates that the incorporation of functionalized CNMs into Spiro-OMeTAD can significantly enhance both the performance and stability of PSC devices.



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Rational Design of Fluorescent Glycofullerenes for Single - Particle Tracking

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Fullerenes are a class of carbon-based nanomaterials with significant potential as biocompatible platforms, owing to their unique structural properties. The three-dimensional, spherical shape of fullerenes facilitates flexible and well-defined functionalization, while their entirely carbon-based structure ensures biocompatibility, stability, and biodegradability. Glycofullerenes, in particular, have been shown to mimic viruses such as Ebola, Zika, and SARS-CoV-2 by interacting with cellular lectins, including the DC-SIGN receptor, thus blocking viral infection.¹⁻³

The aim of this study is to synthesize and characterize the photophysical properties of multichromophoric, fluorescent, and multivalent glycofullerenes to investigate their interactions with viral receptors at the single-particle level.⁴ To this end, we employ a rational design strategy using click chemistry to build dendrimeric scaffolds consisting of a fullerene core, 12 BODIPY molecules arranged symmetrically, and 24 mannose residues that serve as multivalent ligands for lectin receptors (**FIGURE**).

The development of highly emissive fullerene-based multichromophoric compounds holds great promise for advancing fluorescence microscopy and single-particle tracking, offering new insights into the mechanisms of viral inhibition.

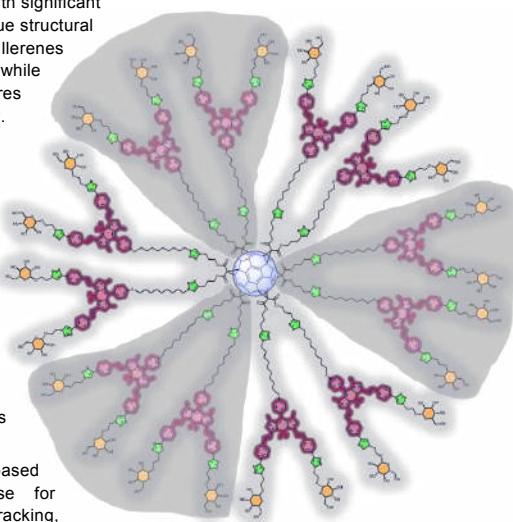


FIGURE: DC-SiGN binding fluorescent glycofullerene

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Truxene for sensing of contaminants

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Sensing analysis plays a crucial role across various sectors such as chemical industry, human health diagnostics, environmental and food safety. Environmental pollutants like explosives, heavy metal ions, antibiotics and others means significant risk to human health. As a consequence, the search for a better method for the detection of these environmental pollutants has increased in recent years.¹ Conjugated microporous polymers (CMPs) have recently emerged as very promising candidates for various applications due to their convenient chemical modularity, remarkable thermal and chemical stability and persistent porosity.² Their luminescent properties have proven to be effective in detecting analytes of interest through enhanced electronic and optical responses. In addition, the interaction of their π -conjugated systems with light underpins their photocatalytic detoxification activity, as demonstrated by novel semiconducting porous polymers.³ In this communication, we present our results of different Truxene-based porous organic materials for supramolecular detection of different contaminants such as antibiotics in water or explosives in organic solvents.

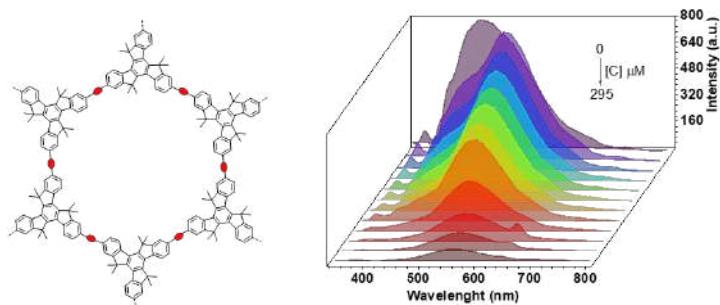


Figure: Structure of Truxene base porous organic polymer and sensing turn-off.

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Rational Design of Color-Pure Blue Organic Emitters by Poly-Heteroaromatic Omni-Delocalization

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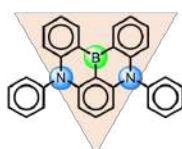
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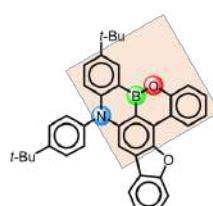
Current research on organic light emitters which utilize multiple resonance-induced thermally activated delayed fluorescence (MR-TADF) materials is gaining significant interest because of the materials' ability to efficiently generate color-pure blue emission. However, the underlying reasons for high color purity remain unclear. It is shown here that these emitters share a common electronic basis, which is deduced from resonance structure considerations following Clar's rule, and which is termed as "poly-heteroaromatic omni-delocalization" (PHOD). The simple and clear design rules derived from the PHOD concept allow extending the known chemical space by new structural motifs. Based on PHOD, a set of novel high-efficiency color-pure emitters with brilliant deep-blue hue is specifically designed.^[1]

Poly-Heteroaromatic Omni-Delocalization

60° annelated

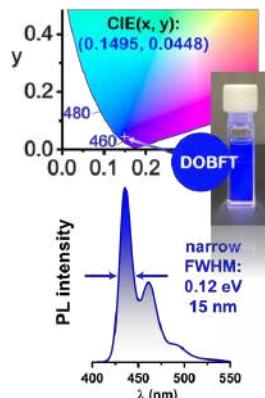


90° annelated



DABNA-1

DOBFT



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Impact of Molecular Weight on the Electronic Properties and Performance of Conjugated Polymers in Optoelectronic Devices

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The molecular weight (MW) of conjugated polymers significantly influences their electronic properties, impacting their performance in optoelectronic devices such as organic solar cells, light-emitting diodes, and field-effect transistors. This study explores the dependence of key electronic properties—charge transport, optical absorption, energy level alignment, and morphological behavior—on the molecular weight of conjugated polymers. High-MW polymers generally exhibit enhanced charge carrier mobility due to improved π - π stacking and greater chain entanglement, promoting efficient charge transport pathways. Conversely, low-MW polymers often lead to better solubility and processability but at the cost of compromised electronic properties. The balance between molecular weight, structural order, and processability is examined to provide insights into optimizing polymer design for specific device applications. By correlating molecular weight to critical parameters such as crystallinity, domain purity, and energy band alignment, this work highlights strategies for tailoring conjugated polymer performance through precise molecular weight control.

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Biphasic Electron Transfer Unambiguously Revealed in C343 Sensitized Mesoporous SnO₂ by a Combination of Fluorescence Up-Conversion Spectroscopy (FLUPS) and Time-Resolved Terahertz Spectroscopy (TRTS)

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Dye-sensitized metal oxide (dye-MO) films are a promising technology in the field of solar energy conversion. At the dye-MO interface, a fundamental parameter is the electron transfer (ET), an electron injection from the lowest unoccupied orbital level of the dye to the conduction band (CB) of the MO. However, the kinetic competition between the ET and other relaxation channels largely determine the efficiency in complete devices. Since both the signals arising from an ET process and those linked with detrimental kinetical deactivation channels have an exponential fingerprint, it is still challenging to unambiguously characterize ET lifetimes.

In this work, we have combined Fluorescence Up-Conversion Spectroscopy (FLUPS) [1] and Time-Resolved Terahertz Spectroscopy (TRTS) [2] to remove any ambiguity in the determination of the ET mechanism in a dye-MO model system, a Coumarin 343-Tin Oxide (C343-SnO₂) film. FLUPS is mostly sensitive to the photoexcited electron population in the dye, while TRTS reveals the injected electron population in the MO. Applied at the C343-SnO₂ interface, the combination of FLUPS and TRTS allows us to unambiguously resolve two independent ET channels with lifetimes and relative amplitudes quantitatively matching within error: ~1.4 ps and ~17.0 ps, whose relative amplitudes are (77±5)% and (23±5) %, respectively. Our approach offers a reliable criterion for the characterization of sensitized systems, and hence will contribute to a better understanding of photoinduced interfacial dynamics in the dye-MO films technology.

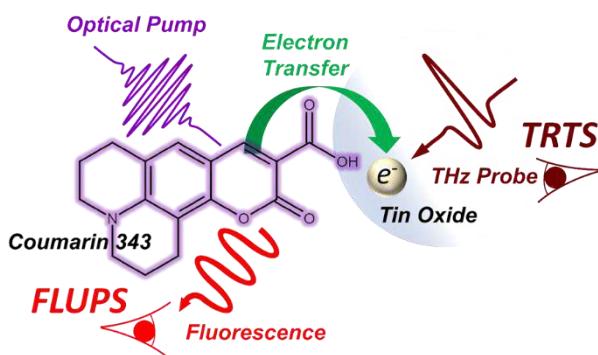


Figure 1. Scheme of combined FLUPS and TRTS measurements on C343-SnO₂ films. After pump photoexcitation (purple), by FLUPS we probe the dye-metal oxide film from C343-donor perspective through changes in the fluorescence trace (red) before and after sensitization of the SnO₂ layer, when a competing pathway emerge, ET (green dark arrow). On the other side, TRTS, which characterize the film from SnO₂-acceptor perspective, determine the photoconductivity from SnO₂ conduction band through a THz probe beam (dark brown).

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