BOOK OF ABSTRACTS

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Foreword

On the 11th day of September 2024, a Portuguese, a Spanish, and a French photochemist walked into a conference... and over the course of three days at the Academia das Ciências de Lisboa, a vibrant scientific exchange unfolded.

The VIII Jornadas Ibéricas de Fotoquímica (8'JIF) and the I Franco-Iberian Conference on Photochemistry (1'FICP) brought together a vibrant community of 110 participants at the Academia das Ciências de Lisboa for an engaging and fruitful scientific exchange. With 91 scientific contributions, including 3 plenary lectures, 17 invited lectures, 31 oral communications, and 39 poster presentations, this edition was a testament to the growing interest and collaboration in the field of photochemistry.

Throughout the conference, participants delved into the latest advancements, exploring a diverse array of topics in both fundamental and applied photochemistry. The high level of engagement, productive discussions, and the spirit of collaboration highlighted the success of this gathering. The atmosphere was one of shared curiosity and mutual learning, fostering an environment where new ideas could flourish.

We were also delighted to celebrate outstanding contributions through two awards: Saül Garcia Orrit received the prize for Best Poster Presentation, and Eloe Dubus was honored with the award for Best Oral Communication. These recognitions, sponsored by Chemistry Europe, highlight the quality and innovation present throughout the event.

We extend our deepest gratitude to our sponsors, whose support was invaluable in making this event possible.

As the 8th edition of this esteemed conference series, this was the first time we had the pleasure of including our French colleagues in the Jornadas Ibéricas de Fotoquímica. Their participation added tremendous value, enriching discussions and broadening the scope of scientific exchange. The success of this joint effort highlights the strength and potential of collaboration between the Portuguese, Spanish, and French photochemistry communities. We hope that this spirit of cooperation will continue and grow in future editions, further advancing the frontiers of photochemistry.

Thank you to all the participants, speakers, and organizers who contributed to the success of this conference. We hope that the knowledge exchanged and the connections made here will continue to inspire and propel our field forward.

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PLENARY LECTURES

INVITED LECTURES

ORAL COMMUNICATIONS

POSTER PRESENTATIONS

Plenary Lectures

PL1

Supramolecular photochemistry, from fundamentals to applications

Dario M. Bassani[1]*

[1]Inst. of Molecular Sciences, Univ. of Bordeaux and CNRS UMR 5255, Talence, France
*dario.bassani@u-bordeaux.fr

With the promise of new systems for sensing and energy conversion, focus in molecular electronics has shifted to supramolecular materials possessing extended structures with delocalized orbitals. Beyond the goal of replacing high criticality rare-earth metals, the use of supramolecular interactions opens new opportunities to test properties that may eventually lead to emerging applications. This presentation will explore various means of exploiting supramolecular interactions to control the behavior of excited states. For example, it is possible to design systems in which specific components will either mix or de-mix.[1] The latter case is an example of narcissistic self-sorting and can be used to enhance the color separation in ultra-high resolution RGB OLED devices.[1] The approach is modular, and different systems incorporating specific properties (eg TADF or CPL behavior) can be combined using inkjet printing to prepare functional supramolecular electronic devices.[2]

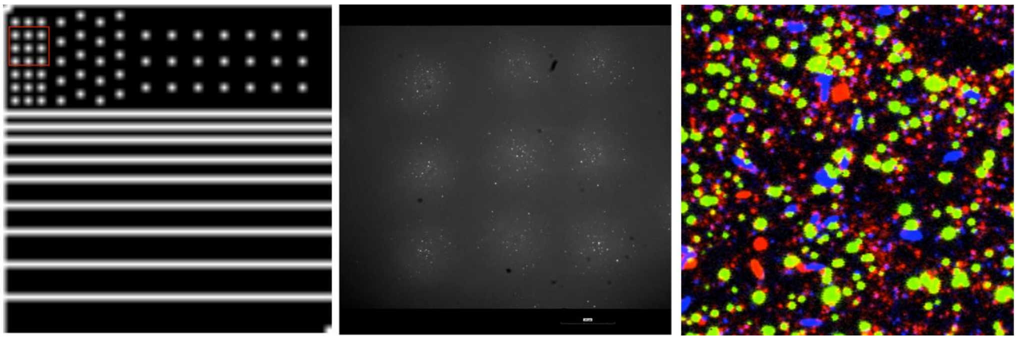

Figure. *Inkjet-printed OLEDs using supramolecular aggregates (left) and close-up of individual drops (center). Right: OLED device incorporating RGB colors that do not mix for super-high-resolution applications.*

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PL2

Use of heavy metal atoms for triplet harvesting. Room temperature phosphorescence, singlet oxygen production and supramolecular assemblies

Laura Rodríguez[1]*

[1]Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain.

* *laurarodriguezr@ub.edu*

Au(I) and Pt(II) compounds are of great relevance from different points of view. They present, in general, linear geometries in the case of Au(I) and square planar for Pt(II) derivatives. Their properties are driven by the organic ligands coordinated to the metal and by the possible establishment of weak intra- or intermolecular contacts.
Having this in mind, in our research group we are focused on the design and synthesis of the suitable organic ligands that can be monodentate (in the case of Au(I) derivatives) or monodentate + tridentate (in the case of Pt(II) complexes) and their coordination to the corresponding metal atom. We analyze the resulting luminescent properties and their applications in the fields of supramolecular chemistry, luminescent materials, singlet oxygen production, luminescent chemosensors or biological activity among others. These properties can be modulated and affected by the formation of supramolecular interactions. Interestingly, we can modulate the possible assemblies to obtain structures with different sizes and shapes, what is a challenge for photophysics and supramolecular point of view and even more, trying to have a control on it.[1] Additionally, with the correct choice of the chromophore, we can also tune the resulting colors and emission intensities that come from the aggregation.[2]

In the last years, we are also focused on the development of room temperature phosphorescence emitters and $^1O_2$ photosensitizers.[3] This is an important challenge from different type of applications such as in OLED devices.

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PL3

Water's Hidden Density Dance

Luís D. Carlos*

Phantom-G, CICECO-Aveiro Institute of Materials, Physics Department, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

* *lcarlos@ua.pt*

The emergence of luminescent nanothermometry during the last decade opened the possibility of measuring thermal flows at spatial scales below 1 µm, unreachable by conventional electrical methods. Diverse phosphors capable of providing remote detection through their light emission properties have been examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, and trivalent lanthanide (Ln3+) ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometer nanoplatforms, upconverting, downconverting and downshifting nanoparticles.[1]

In recent years, luminescence nanothermometry has entered a more mature stage. Although new classes of thermographic phosphors continue to be reported (e.g., covalent organic frameworks and single-ion magnets) we are perceiving a gradual shift in the emphasis of the technique. The research efforts are now focused on establishing comprehensive theoretical backgrounds and standardization procedures (both in data acquisition and processing and in measurement methodologies), discussing the reliability, repeatability, and reproducibility of the technique, and developing new applications.[1]

In the lecture, we will discuss the intricate relationship among temperature, pH, and Brownian velocity in a range of differently sized upconversion nanoparticles dispersed in water. These nanoparticles, acting as nanorulers, offer insights into assessing the relative proportion of high-density and low-density liquid in the surrounding hydration water, validating the two-state model. These findings underscore the significance of the surface of suspended nanoparticles for understanding high- to low-density liquid fluctuations and water behavior at charged interfaces.[2,3]

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Invited Lectures

IL1

Controlling chemical reactivity with light using molecular photoswitches

Jordi Hernando*

Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès (Spain)

**jordi.hernando@uab.cat*

Thanks to the advantages that light provides as an external stimulus, the development of photoinduced chemical processes paves the way to control *when* and *where* chemical reactivity takes place. A very appealing way to accomplish this goal is by introducing molecular photoswitches into the structure of reagents and catalysts, which could then be toggled between reactive and nonreactive states upon irradiation.[1,2] As a result, chemical processes could be started and stopped on demand with extremely high spatiotemporal precision, a behavior that can be exploited in a variety of fields ranging from polymer synthesis[3] to photolithography[4] and 3D printing.[5]

In this presentation I will present some of the latest work conducted in our group in the field of light-controlled chemical reactivity with molecular photoswitches. To reach this purpose, we aim to take advantage of the electronic changes that occur when photoisomerizing between the ring-open and ring-closed states of diarylethenes switches,[6] a concept that we have applied to three main areas: (a) the preparation of photoswitchable phosphine ligands for light-regulated metal catalysis;[7,8] (b) the development of new photoligation reactions based on photoswitchable reagents;[9] and (c) the optical control of polymer network formation.

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IL2

Photophysics and Devices of Platinium(II) Complexes Showing Intense, Excimer Like, Near-Infrared Luminescence.

Piotr Pander,[1,2] Amit Sil,[3] Rebecca J. Salthouse,[3] Christopher W. Harris,[3] Melissa T. Walden,[3] Dmitry S. Yufit,[3] Ruth Daniels,[4] Ashleigh Horn,[4] Andrey V. Zaytsev,[4] Valery N. Kozhevnikov,[4] J. A. Gareth Williams,[3] and Fernando B. Dias.[2]*

[1]Faculty of Chemistry, Silesian University of Technology, & Centre for Organic and Nanohybrid Electronics, Silesian University of Technology, Poland.
[2]Department of Physics, Durham University, Durham, DH1 3LE, UK.
[3]Department of Chemistry, Durham University, Durham, DH1 3LE, UK.
[4]Department of Applied Sciences, Northumbria University, Ellison Building, Newcastle upon Tyne, NE1 8ST, UK.

**f.m.b.dias@durham.ac.uk*

Efficient near-infrared (NIR) emitters, crucial for technologies like NIR-OLEDs, face challenges due to reduced emission efficiency compared to visible counterparts. The energy gap law exacerbates these limitations by linking non-radiative transition probabilities to energy state separation. As emission shifts towards longer wavelengths, energy dissipation increases, leading to rapid non-radiative decay and diminished luminescence. Developing strategies to overcome the effects of the energy gap law remain, therefore, crucial to improve performances of dyes and devices in the low-energy part of the spectrum. Here, we present detailed photophysical studies and theoretical modelling of excited states formed by Pt(II) complexes, which display NIR photoluminescence in film and NIR electroluminescence in OLEDs. Insight into the kinetic properties of Pt–Pt excimers in solution, in films processed from solution and in vacuum-deposited films is provided. Showing a clear distinction between emission from dimers and higher oligomers (*e.g.*, trimers and tetramers). An alternative approach to the architecture of OLEDs based on aggregate states of Pt(II) complexes is also demonstrated, where an emissive layer (EML) as thin as 1 to 2 nm can be employed, maintaining efficiency while reducing precious-metal compound usage by over 90%, compared to conventional devices with thicker layers (20–40 nm).

IL3

Molecular upconversion Or How to pile photons in lanthanide complexes

Loïc J. Charbonnière*

Equipe de Synthèse pour l'Analyse (SynPA), Département des sciences analytiques,
Institut Pluridisciplinaire Hubert Curien, IPHC, UMR 7178, CNRS/Université de Strasbourg, France
\l.charbonn@unistra.fr

Upconversion (UC) is the process by which the energy of two or more photons are stored in a compound and restored in the form of luminescence at a higher energy than the excitation beam. Known for more than 60 years for solid compounds,[1] it is only some ten years ago that the first examples were described in discrete molecules at very low temperature (30K) in organic solvents.[2]

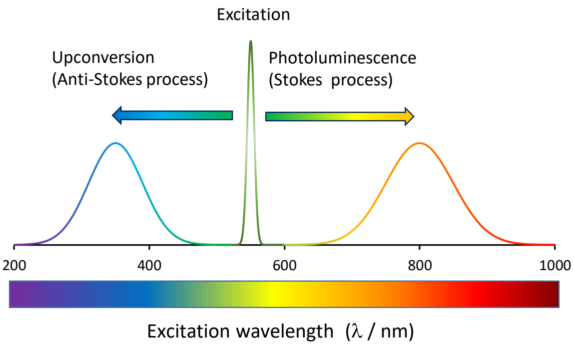

Figure 1: representation of conventional and non-conventional (Anti-Stokes) luminescence process

Through the rational design of heteropolynuclear lanthanide complexes, we succeeded to demonstrate that molecular UC can not only be observed at room temperature,[3] but also in aqueous solvents,[4] and even in pure water,[5] opening the space to a new family of luminescent labels.
Additionally, supramolecular architectures enlarged the perspectives of yet unexplored UC mechanism at the molecular level, such as the observation of cooperative sensitization in Yb/Tb nonanuclear clusters,[6] cooperative sensitization of Yb dimers,[7] or Yb to Ru UC energy transfer in hetero-polynuclear d-f complexes.[8] This presentation will provide a little journey into molecular UC.

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IL4

Smart Luminescent Peptide-based Biosensors for Probing Kinase Activity

Juan A. González-Vera[1]*, Carmen Salto-Giron[1], Francisco Fueyo-González[2], Angelica MartínPriego[1], A. Reinoso-Rodríguez[3], Miguel Fribourg[2], Angel Orte[1]

[1]Nanoscopy-UGR Laboratory. Faculty of Pharmacy. University of Granada. Campus Cartuja, Granada 18071, Spain

[2]Translational Transplant Research Center, Division of Nephrology, Department of Medicine, Icahn School of Medicine at Mount Sinai, New York, NY 10029, USA

[3]Department of Biochemistry and Molecular Biology II. Faculty of Pharmacy. University of Granada. Campus Cartuja, Granada 18071, Spain

gonzalezvera@ugr.es

Phosphorylation triggered by extracellular signals and carried out by protein kinases is a fundamental signal transduction mechanism involved in the regulation of most basic processes in eukaryotic cells. Unfortunately, diagnostic approaches for detecting alterations in these kinase activities in a standardized fashion are poorly developed, and they involve indirect and invasive approaches. Consequently, sensitive and selective tools for monitoring kinase activities are of great importance, not only in the process of drug discovery, but also for unraveling the diverse signaling cascades in which these enzymes are pivotal. Today, there is an urgent need for innovative sensing technologies, which would allow for sensitive, rapid and non-invasive detection of protein kinases *in situ*. Peptide-based biosensors that rely on luminescence changes upon phosphorylation are highly desirable, because these systems allow a continuous readout, offering an excellent spatial and temporal resolution to observe in real time kinase activity in a sensitive, timely, and non-invasive fashion.[1,2]

We have initiated a program aimed at developing a family of smart luminescent biosensors, specifically designed to provide quantitative information using flow cytometry and advanced multidimensional microscopy techniques, such as photoluminescence (PL) lifetime imaging microscopy (PLIM) and super-resolution nanoscopy.[3] These smart sensors have been successfully implemented to probe *in vitro* and *in cellulo* the realtime activity of several kinases critical for cell function and activation.

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IL5

Delocalized lipophilic cations for mitochondrial targeting and other applications

Francisco Galindo *

Universitat Jaume I de Castellón, Departamento de Química Inorgánica y Orgánica, Av. V. Sos Baynat s/n, 12071 Castellón de la Plana, Spain

* *francisco.galindo@uji.es*

Recently, there has been increasing attention on the development of organic molecules designed to selectively accumulate in specific organelles, especially the mitochondria,[1] either for visualization with enhanced resolution and selectivity or for therapeutic purposes. One characteristic commonly found in many mitochondrial probes described thus far is the presence of a positive charge delocalized along an extended organic scaffold. As a result, the term "delocalized lipophilic cation" (DLC) is used in the literature to classify this class of mitochondria-targeting structures.

Over the past decade, our group has focused on studying a series of DLCs with the aim of targeting mitochondria in living cells and detecting the presence of biologically relevant biomolecules inside this organelle, particularly nitric oxide. This presentation provides an overview of these investigations, highlighting not only the developed sensors for bioimaging (see Figure) but also unexpected applications found in other technological fields.[2]

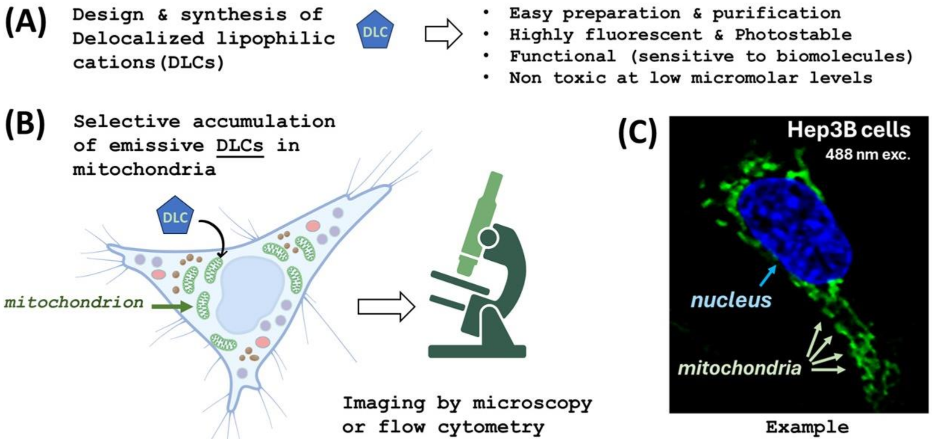

Figure. *Schematic representation of the process of studying DLCs in the biological context: (A) design and synthesis, (B) studies in living cells using optical methodologies, (C) a representative example from our own research.*[2d]

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IL6

Optical properties of 0D nanocarbons.

Ermelinda Maçôas[1]*, Carla I. M. Santos[1,2], M. J. Álvaro-Martins,[1] C. M. Cruz,[2] Sandra Míguez-Lago,[3] Juan M. Cuerva,[3] Araceli G. Campaña[3]

[1] Centro de Química Estrutural and Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

[2] LAQV–REQUIMTE and Department of Chemistry, University of Aveiro, 3810–193, Aveiro, Portugal

[3] Departamento de Química Orgánica, Universidad de Granada (UGR), C. U. Granada, Spain

* *Ermelinda.macoas@tecnico.ulisboa.pt*

The nonlinear optical properties of 0D nanocarbons have been explored in optoelectronic and photonic devices and in biomedical applications. However, the limited number of studies that focus on nonlinear absorption, the large dispersion of quantitative data reported in literature, and the poor structural characterization of the materials, prevent translation of research results into truly impactful solutions. Systematic studies are needed for unambiguous definition of the design guidelines to produce materials with high nonlinear response in a reproducible and scalable way. This presentation focusses on recent work on the nonlinear optical properties of 0D nanocarbons produced by three different approaches: bottom-up amorphous carbon dots (Cdots), top-down graphene quantum dots (GQD) and step-by-step controlled organic synthesis of distorted nanographenes (NG).[1-3] The low emission yields of oxidized 0D nanocarbons produced by top-down or bottom-up methods is discussed, it is shown that the two-photon cross-section of the carbon core is not as high as initially anticipated and that, to some extent, distortion of the sp^2 network can improve the nonlinear optical properties.

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IL7

Tailoring metal halide perovskites and related nanomaterials for light-driven applications

Raquel E. Galian*

Institute of Molecular Science, University of Valencia, c/ Cat. José Beltrán 2, Paterna, 46980, Valencia, Spain
* *raquel.galian@uv.es*

Perovskite nanocrystals (NCs) are well known for their exceptional tunable optical and electronic properties. They can be engineered at the nanoscale to optimize their interaction with light, improving the efficiency of the absorption, transfer, and conversion of energy. In this context, the ability of colloidal $CsPbBr_3$ NCs to act as efficient photosensitizer and photocatalyst will be presented (Figure 1). Their photocatalytic activity for organic chemical transformation will be compared with that of lead-free metal halide $Cs_3Sb_2Br_9$ NCs, highlighting the key role of the surface chemistry in facilitating the interaction between the NC and the substrate. [1,2] Furthermore, the merging of $CsPbBr_3$ NC with photoactive BODIPYs, can modulate the photophysics of the corresponding NC@BODIPY nanohybrid. The potential of I2-BDP dyes to extract the hot hole carrier was used as energy transfer photocatalyst for oxidizing α-terpinene to ascaridole.[3,4] These findings underscore the potential of hybrid materials to enhance the capability of light-driven processes.

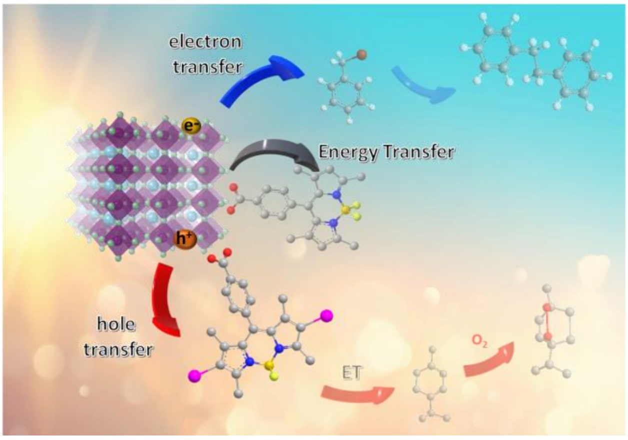

Figure 1. *Illustration of perovskite NCs as photosensitizer / photocatalyst for visible-light harvesting applications.*

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Acknowledgement

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IL8

Photodetachment of Chlorophyll species in gas phase

Niloufar Shafizadeh*

Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS UMR 8214 - Université Paris Saclay , 91405, Orsay, France

**niloufar.shafizadeh@cnrs.fr*

For a better understanding of the photosynthesis mechanism, it is important to know precisely the vibrational and vibronic structure of different chlorophyll pigments in the gas phase. To achieve this goal, we use electron photodetachment spectroscopy of cooled anions. The properties of the anion are characterized by measuring the kinetic energy of the electron ejected after photoexcitation.

We have built a new experimental setup coupling a nonoelectrospray, a cooled ion trap with a photoelectron detection. The first step of this work is to determine the most stable deprotonation sites of several Chlorophyll pigments in gas phase. I will show that the photodetachment can be applied to identify the deprotonation site and discriminate between different deprotonomer. I will also show our first attempt to assign pheophorbide virational modes.

IL9

Seeing is believing: microscopic techniques to uncover cell-matrix interactions in biomimetic hydrogels

Susana Rocha*

Molecular Imaging and Photonics, Chemistry Department, KU Leuven, Leuven, Belgium

* *susana.rocha@kuleuven.be*

Understanding the complex interplay between cells and their surrounding matrix is paramount for advancing biomimetic scaffold design. By pushing and pulling on the extracellular matrix (ECM), cells continuously sense the dynamic mechanical cues from their environment and generate mechanical feedback. Mechanical characterization of the matrix surrounding the cells has shown that contractile cells can generate a stiffness gradient in biological gels. Such cell-generated forces can reorganize and deform the natural ECM fibers, causing fiber densification and alignment. Traditional methods like electron microscopy and scanning probe microscopy provide high spatial resolution but fall short in capturing these dynamic processes in situ. This talk highlights the use of fluorescence microscopy to characterize the structure of synthetic hydrogels and quantify the traction forces generated by the cells.

We use confocal imaging and bead-free traction force microscopy (TFM) to demonstrate how a fully synthetic biomimetic hydrogel can be used as a platform for exploring the influence of biochemical and mechanical factors on cell-matrix interactions. This biomimetic hydrogel, formed from oligo(ethyleneglycol)-functionalized polyisocyanate (PIC) polymers, is formed by non-covalent interactions and exhibits a nonlinear mechanical response at low stresses.

We further investigate the forces that cells apply at a molecular scale using FRET-based tension sensors. These sensors allow us to measure the molecular-scale forces exerted by the cells, providing insights into how cells interact with and remodel their microenvironment. Our fluorescence microscopy-based approach sheds light on how physical cues regulate cell-matrix interactions, offering insights applicable to other hydrogels.

IL10

The beauty of photoelectrochemical conversion of solar energy through organic polymer-based hybrid systems

Mariam Barawi[1]*, Javier Llorente[1], Sandra Palenzuela[1], Miguel Gómez[1], Miguel García Tecedor[1], Freddy Oropeza[1], Ignacio J. Villar-García[2], Marta Liras[1], Víctor A. de la Peña O´Shea

[1] Photoactivated Processes Unit IMDEA Energy Institute, Av. Ramón de la Sagra 3, 28935 Móstoles, Madrid, Spain.

[2] CEU San Pablo University, Chemistry Department, Faculty of Farmacy, Urbanización Montepríncipe, 28668, Boadilla del Monte, Madrid, Spain.

* *mariam.barawi@imdea.org*

Solar energy conversion via photoelectrochemical (PEC) cells offers a promising solution to current energy challenges, but significant advancements in materials and cell configurations are necessary. Organic polymers, particularly conjugated polymers (CPs), show potential due to their light-harvesting and conductive properties. However, linear CPs often face stability issues in water under prolonged light exposure. Conjugated porous polymers (CPPs), with their 3D structure, provide improved stability, catalytic properties, and higher surface area, yet their synthesis typically yields large-particle powders unsuitable for thin film preparation. Combining semiconductors can enhance light absorption and prevent charge recombination, but widely studied materials like TiO2 suffer from limited visible light absorption due to their high bandgap energy.

In this work, we introduce innovative strategies to enhance the efficiency of CPPs in PEC cells. First, we employ mini or ultra-mini emulsion synthesis to produce particles ranging from 500 nm to 20 nm, ideal for thin film preparation. Second, we design monomers tailored for electropolymerisation, resulting in high-quality thin films with precise thickness control. These approaches enable comprehensive characterization of CPPs' optoelectronic properties, ensuring stability and high film quality over time. Several polymers have been synthesized, and their electronic structures determined using XPS, electrochemistry, and UV-VIS spectroscopy, demonstrating their suitability as photoelectrodes.

The hybrid photoelectrodes undergo thorough characterization via X-ray diffraction, SEM, EDX, and AFM. A suite of photoelectrochemical assessments, including linear scan voltammetry, chronoamperometry, and photopotential measurements, underscores their potential for solar energy conversion. These hybrid photoelectrodes exhibit superior photovoltages and photocurrents compared to TiO2 and CPP alone, confirming robust light absorption and efficient charge transfer. Electrochemical impedance spectroscopy (EIS) and Transient Absorption Spectroscopy (TAS) further validates enhanced charge transfer in the illuminated hybrid photoelectrodes. Finally, a Proof of concept Tandem PEC cells, connected to a gas chromatograph, demonstrate and quantify hydrogen generation, highlighting their effectiveness in solar energy conversion.

IL11

Organometallic Catalysis under Visible Light

Louis Fensterbank[1,2]*

[1] Institut Parisien de Chimie Moléculaire, Sorbonne Université, 4, place Jussieu, 75005 Paris
[2] Collège de France, 11 place Marcelin Berthelot, 75005 Paris
*louis.fensterbank@college-de-france.fr

The Over the last decade, we have been involved in the implementation of organometallic catalysis to the development of sustainable radical chemistry. We have introduced bis-catecholato silicates as versatile sources of alkyl radicals upon photocatalysis.[1] Using Ir(III) or organic photocatalysts, alkyl radicals can be engaged in intermolecular reactions. This process can be merged with Ni-catalyzed C_{sp2}-C_{sp3} cross-coupling reactions. In parallel, and following our interest in gold catalysis, our recent efforts in photoredox/gold dual catalysis will also be presented.[2] We have notably evidenced the first examples of photosensitized oxidation additive to a gold(I) complex leading to C_{sp2}-C_{sp} cross-couplings.[3,4]

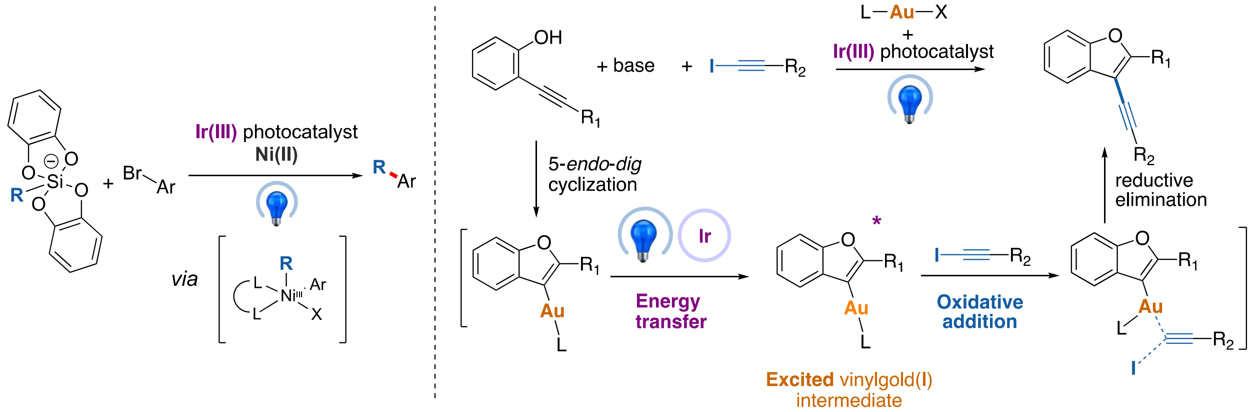

Figure. Photo-organometallic dual catalysis

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IL12

New functional inorganic materials for the prevention of pollution in heritage materials and urban habitat

Adrián Pastor*

Departamento de Química Inorgánica e Ingeniería Química, Instituto Universitario de Nanoquímica IUNAN, Universidad de Córdoba, Campus de Rabanales, E-14014, Córdoba, Spain

* *q92paesa@uco.es*

The Thesis deals with the photocatalytic removal of nitrogen oxides gases (NO_x) from the urban atmosphere ($DeNO_x$ action). These gases are one of the most important air pollutants, provoking damage in heritage buildings and human health. A sustainable way to remove NO_x is photocatalysis, where NO_x are oxidised using the photocatalyst, sunlight, and atmospheric water and oxygen. Photocatalytic building materials (such as cements, paints, pavements) with a $DeNO_x$ effect are currently on the market, but these are not widely used in urban architecture due to several limitations of the used photocatalytic additives. The thesis focuses on inorganic compounds that are easy to prepare, sustainable and economical, to obtain additives with adequate properties. Three strategies were followed (Fig. 1). Briefly, rice husk was used for the preparation of ZnO-based photocatalysts by a simple methodology (dry mixing + calcination), showing high $DeNO_x$ photocatalytic performance (70%)[1]. In another work, the Fe^{3+} doping of a Layered Double Hydroxides (LDHs) was studied to improve the $DeNO_x$ performance. The incorporation of the iron cation in the LDH structure created new pathways for deactivating photocharges, the $DeNO_x$ photocatalytic performance being the highest reported for an LDH (59%)[2]. In another study, the application of a special type of LDHs (AMO-LDHs) as $DeNO_x$ photocatalysts was studied. In this sense, it was the first time that an AMO-LDH was used as a photocatalyst, and the AMO-LDHs exhibited extremely high specific surface values (492 m^2g^-1) never reported for these samples, resulting high $DeNO_x$ performance (58%)[3]. All studied samples in the Thesis beat the $DeNO_x$ performance of TiO_2 P25 benchmark (41%) and could be used repeatedly (3-4 cycles) and for long irradiation times (6 h), an optimal period for their application in materials from the urban environment.

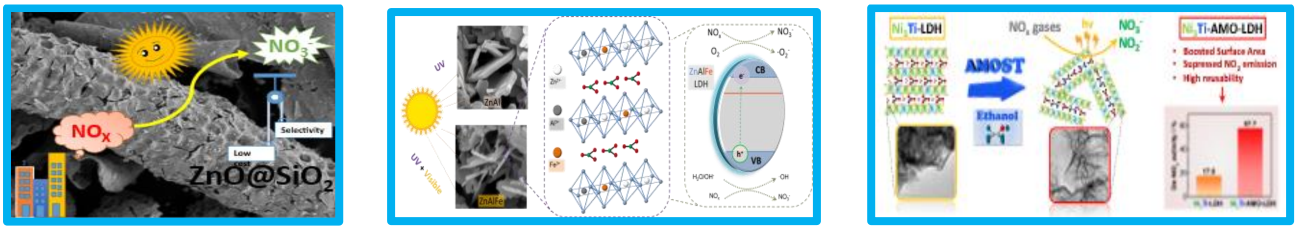

Figure 1. *Investigated $DeNO_x$ photocatalysts: Left : $ZnO@SiO_2$ composites. Centre: $Zn_4Al_{1-x}Fe_x$ LDHs. Right: AMO-Ni_3Ti-LDHs*

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IL13

Photoacoustics in Action

C. Serpa[1,2]*, J. Santos[2], D. A. Pereira[1], C. P. João[2], L. C. Gomes-da-Silva[1], L. G. Arnaut[1,2]
[1]CQC-IMS, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[2]LaserLeap Technologies, Rua Coronel Júlio Veiga Simão, CTCV, Edifício B, 3025-307 Coimbra, Portugal
* *serpasoa@ci.uc.pt*

The generation and application of photoacoustic waves (PAWs) through the conversion of pulsed light into pressure waves have a rich history spanning over a century. Initially serving analytical and imaging purposes, photoacoustic technologies have made significant strides in medical diagnosis and are now extending into therapeutic applications. We present insights from recent advancements in PAW applications for therapy, including gene transfection and tumor priming, highlighting their transformative potential in medicine.

Recent developments have showcased the potential of PAWs in treating various diseases by triggering biological processes and enhancing drug delivery. PAWs are particularly effective in dermatology, oncology, and cardiovascular treatments. For instance, broadband PAWs can transiently permeabilize the skin, enhancing the delivery of large molecules like hyaluronic acid for cosmetic treatments, as well as small molecules such as ascorbic acid derivatives for dermatological applications. Clinical trials have demonstrated significant improvements in skin treatments, including wrinkle reduction and increased topical delivery efficiency. Moreover, PAWs have shown promise in oncology by improving the infiltration of macromolecules, including antibodies, into solid tumors. This enhancement could potentially increase the efficacy of photodynamic therapy and immunotherapies, which are pivotal in cancer treatment but often limited by poor drug delivery to tumor cells, as solid tumors, characterized by a dense extracellular matrix and hypoperfusion, present significant barriers to effective drug delivery. To enhance drug delivery in resistant tumors like 4T1, PAW priming has been employed. Experiments demonstrated that exposing solid tumors to PAWs enhances the distribution of therapeutic agents, thereby improving treatment outcomes. For example, Redaporfin showed higher accumulation in CT26 tumors compared to 4T1 tumors, correlating with better therapeutic efficacy. This approach has also shown potential in delivering large-size biological therapeutics, such as antibodies used in immunotherapy.

Gene transfection, a process of introducing foreign DNA into cells, has seen advancements using PAWs generated by carbon-based piezophotonic materials. These materials, such as graphene and gold nanoparticle-decorated graphene, generate ultrasound pulses with high peak pressures and broad bandwidths, facilitating the permeabilization of cell membranes. This method has achieved a 10% efficiency in transfecting COS-7 cells with a plasmid encoding Green Fluorescent Protein (GFP), without inducing cytotoxicity.

The development of novel photoacoustic transmitters with different materials and source configurations, and remarkable capacity to generate high-amplitude, high-frequency ultrasound pulses enable the integration of photoacoustic technologies in therapeutic and diagnostic applications and marks a significant advancement in medical science. The ability of PAWs to permeabilize biological barriers, enhance drug delivery, improve gene transfection efficiency or microscale fragmentation of solid materials opens new avenues for treating a variety of diseases.

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IL14

Photosensitized nanosystems for targeted Photodynamic Therapy

Virginia Martínez-Martínez[1]*, Ruth Prieto Montero[1], Andrea Albaya[2], Itziar Polanco[3]: Alejandro Prieto-Castañeda[1,4]; Teresa Arbeloa[1]; María J. Ortiz[4]; Alberto Katsumiti[3], Mónica L. Fanarraga[5] and Jose Luis Chiara[2]

[1]Departamento de Química Física, Universidad del País Vasco-EHU, Facultad de Ciencia y Tecnología, Barrio Sarriena s/n, 48940, Leioa, Spain.
[2]Instituto de Química Orgánica General (IQOG-CSIC), Juan de la Cierva 3, 28006, Madrid, Spain.
[3]GAIKER Technology Centre, Basque Research and Technology Alliance (BRTA), 48170, Zamudio, Spain
[4]Departamento de Química Orgánica, Facultad de CC, Químicas, Universidad Complutense, 28040 Madrid
[5]Grupo de Nanomedicina-IDIVAL, Universidad de Cantabria, Herrera Oria s/n, CP 39011 Santander, Spain.
* *virginia.martinez@ehu.eus*

Photodynamic therapy (PDT) is a minimally invasive procedure in which under suitable light irradiation a sensitive drug (photosensitizer, PS) is activated and generates Reactive Oxygen Species (ROS), mainly singlet oxygen (1O2), a cytotoxic species able to damage the nearby cells, virus or bacteria. The interest to implement this therapy against cancer diseases and/or as antimicrobials has increased in the last few years. Although there are many different photosensitizers, most of them are not adequate for their biomedical use because of their poor aqueous solubility or their lack of selectivity for their area of interest. Nowadays, a huge effort is devoted in the development of the third generation of PSs to enhance PDT efficiency. One strategy is based on the design of new operative PSs and an a second alternative approach centred on the use of nanoparticles (NPs) as carriers for PS [1,2].

In this communication, different nanosystems (SN: Silica Nanoparticles, NC: nanoclay and CNC: cellulose nanocrystals) as PS nanocarriers will be presented. These carriers were externally decorated not only with the PS but also with other molecules of interest (PEG, folic acid, sugar derivatives) to improve their aqueous stability and selectivity to cancer cells or bacteria, respectively. They were tested in vitro in HeLa cells and E. Coli bacteria to study their viability for bioimaging and PDT [3,4].

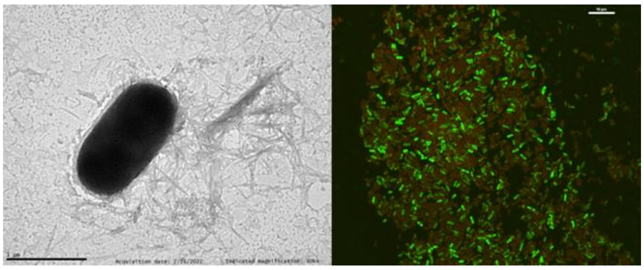

Figure 1. *TEM and fluorescence images of bacteria (E.coli) incubated with PS@CNC*

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IL15

Strategies for the development of Luminescent Solar Concentrators

César A.T. Laia*
LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, FCT-NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
* catl@fct.unl.pt

Luminescent solar concentrators were born as a concept in the 1960's and underwent in depth research during the 1970's.[1] However in the last 20 years the interest towards these devices grew leading to novel applications in the field of solar energy conversion.[2][3][4] In this communication we will also delve into the applications of photonic materials, with a particular focus on Luminescent Solar Concentrators.[5] Inorganic particles are studied including perovskite quantum dots and atom clusters embedded on inorganic float glass. Photoluminescence thin-films deposited on soda-lime glass were studied and proof-of-concepts created about the feasibility of these devices in future applications.

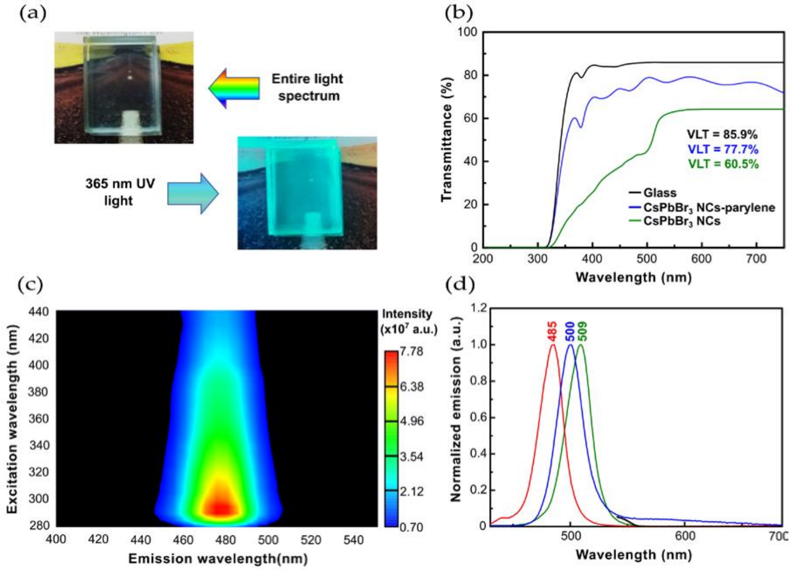

*Figure 1 - Encapsulation of CsPbBr$_3$ NCs thin films with parylene type C: (**a**) coated glass sample under the entire light spectrum and 365 nm UV light; (**b**) impact on the light being transmitted through the glass (black line), when coated with CsPbBr$_3$ NCs thin film (green line), and with the composite film of NCs-polymer (blue line); (**c**) contour plot of the photoluminescence emission intensity at different excitation wavelengths; (**d**) normalized emission spectra of CsPbBr$_3$ NCs in solution (blue line), CsPbBr$_3$ NCs thin film (green line), and CsPbBr$_3$ NCs -parylene thin film (red line).*[5]

This work received support from PT national funds (FCT/MCTES) projects UIDB/50006/2020 and UIDP/50006/2020; the project VIT (H2020-MSCA-RISE-2020 under grant agreement no. 101008237).

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IL16

Light-Induced Charge Accumulation on Iron Porphyrin Catalysts for Photocatalytic CO_2 Reduction

Daniel H. Cruz Neto,[1] Philipp Gotico,[2] Annamaria Quaranta,[3] Winfried Leibl,[3] Karine Steenkeste,[1]
Daniel Peláez,[1] Thomas Pino,[1] Zakaria Halime,[3] Minh-Huong Ha-Thi[1]*

[1] Institut des Sciences Moléculaires d'Orsay (ISMO), Université Paris-Saclay, CNRS, 91405 Orsay – France
[2] Institute for Integrative Biology of the Cell (I2BC), Université Paris-Saclay, CEA, CNRS, 91198 Gif-sur-Yvette – France
[3] Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), Université Paris-Saclay, CNRS, 91400 Orsay – France

* *minh-huong.ha-thi@universite-paris-saclay.fr*

The storage of sunlight in a chemical form has been deemed one of the most promising ways of producing sustainable solar-based fuels. These approaches necessitate efficient ways of capturing sunlight to undergo multiple charge accumulation followed by multielectronic bond formation and breaking catalysis. To achieve this optimization, it is crucial to gain a fundamental knowledge of the detailed mechanistic events occurring during these multielectronic light-driven processes. Time-resolved spectroscopic techniques are powerful tools to investigate the mechanistic aspects of light-driven processes. While intense research efforts are dedicated to elucidate single photoinduced charge transfer processes, to date, only few studies have reported on the characterization of charge-accumulated states on a photocatalytic systems created by sequential photoexcitations, which is a crucial step for catalyst activation.

We utilize an advanced nanosecond optical transient absorption spectroscopic setup with a double excitation to demonstrate, for the first time, the reversible multiple electron accumulation on an active multicomponent catalytic system. This system comprises an urea-modified iron(III) tetraphenylporphyrin catalyst (UrFeIII), the prototypical $[Ru(bpy)_3]^{2+}$ as a photosensitizer, and sodium ascorbate as an electron donor. In the presence of CO_2, the photoreduction was triggered by two charges-accumulated state on the catalyst (UrFeI), leading to the formation of FeII-CO. The novel insights gained from our study on the mechanisms of charge separation and accumulation should stimulate further investigation on the exploration of photocatalytic systems mechanisms, thereby guiding the design of more efficient photocatalysts in the rapidly growing field of solar-to-fuel conversion.

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IL17

Advanced Photocatalysts Lights Up a Bright Future

Joaquim Luís Faria

LSRE-LCM – ALiCE, Faculty of Engineering, University of Porto, Rua Dr Roberto Frias s/n, 4200-465 Porto, Portugal

* *jlfaria@fe.up.pt*

Photocatalysis undoubtedly holds immense potential for addressing various global challenges, particularly in energy production, environmental protection, and health. The long-lasting promises for renewable energy production based on solar fuel generation maintain the community interest in photocatalytic hydrogen generation, artificial photosynthesis, and chemical energy conversion for new vector developments[1,2]. Environmental protection and waste management are essential topics no matter what strategy we adopt in adapting productive processes and materials life cycles to ecosystem shielding. Breaking down organic pollutants in water[3] or degrading volatile organic compounds and nitrogen oxides in the air are at the forefront of a sustainable future in the same pollution reduction measure. Photocatalysts can accelerate the breakdown of plastics into non-toxic compounds, reducing plastic pollution in oceans and landfills, or can be used to degrade harmful pesticides or dyes, protecting ecosystems and improving the safety of food and water supplies[4]. In health and safety applications, we can create self-cleaning and antimicrobial surfaces for use in hospitals and public spaces to reduce the spread of infections[5]. Finally, chemical synthesis can gain whole new relevance by using light to run over pathways not accessible in the traditional thermal activation[6]. Advanced photocatalysts are specifically designed to accelerate and enhance chemical reactions upon exposure to light, ideally visible light. These materials evidence enhanced light absorption (like carbon nitride, g-C_3N_4, which can utilize a larger portion of the solar spectrum than the traditional metal oxides), high quantum efficiency, improved charge separation, stability, durability, and tailored surface properties. Advanced photocatalysts hold the transformative potential for a sustainable and healthy future. By leveraging the power of light, photocatalytic technologies can provide innovative solutions. Continued research and development in this field will be crucial for overcoming current limitations and unlocking the full potential of photocatalysis in a bright future.

This research was supported by national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020).

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Oral Communications

OC1

New Photoactive COFs for the Controlled Release of Guest Molecules

Raquel Gavara[1,2]*, Gonzalo Abellán[1], Fernando Pina[3], A. Jorge Parola[3], Félix Zamora[1]

[1]Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Spain
[2]Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, Spain
[3]LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

raquel.gavara@uam.es

Covalent organic frameworks (COFs) have attained substantial attention in different application areas due to their extraordinary behaviour in tuneable porosity, large surface area, high crystallinity, surface chemistry and recyclability. In this context, there is a growing interest on developing COFs with response to external stimuli. These smarts materials exhibit reversible changes in physical and chemical properties under external stimuli such light and heat and result very attractive in applications dealing with the controlled release of molecules, including drug delivery, self-healing of materials and food preservation, among others.[1]

Flavylium derivatives are a well-known family of photochromic compounds where the photoactive species, the *trans*-chalcone (Ct) is reversibly transformed under irradiation into the coloured species, the flavylium cation (AH^+) and/or quinoidal base (A).[2,3]

In this work, two new photoactive COFs namely, **$Ct_{0.33}$-COF** and **$Ct_{0.17}$-COF** were prepared by pore functionalization of COFs precursors with Ct moieties. The synthetic modification was achieved through the efficient Huisgen's 1,3-dipolar cycloaddition ("click") reaction and the materials were thoroughly characterized regarding their chemical, textural and morphological properties. The pH-dependent photo-transformation of Ct into AH^+ within the pores was studied in aqueous suspensions of the COFs. Finally, the possibility of using these materials for light-controlled release of guest molecules was assessed through studies with the model dyes rhodamine B (RhB) and methylene blue (MB) (Figure 1).

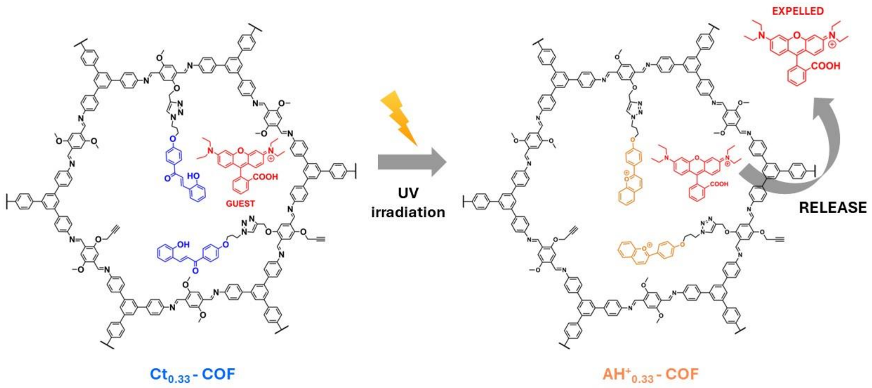

***Figure 1.** RhB release under UV irradiation of **$Ct_{0.33}$-COF** to give **$AH^+_{0.33}$-COF**.*

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OC2

Control of the photochromic reaction of DASA compounds by quantification of the multi-step processes

Éloé Dubus,[1] Julien Mallétroit,[1] Zakaria Ziani,[2] Guy Royal,[2] Keitaro Nakatani,[1] Joanne Xie,[1] Guillaume Laurent,[1] Rémi Métivier[1]

[1] ENS Paris-Saclay, CNRS, PPSM, 91190 Gif-sur-Yvette, France
[2] Université Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France

Email: eloe.dubus@ens-paris-saclay.fr

Recently, "negative" photochromic molecules have been increasingly studied substantially due to their usefulness in various applications (security devices, biological probes or drugs, solar energy storage, etc). [1], [2] Among the negative photochromic families, Donor-Acceptor Stenhouse Adducts (DASA) have especially attracted significant attention for their easy synthesis, intense color (in the dark), and fast photoreaction to complete colorless state (under light). [3]

In this work, we will present a quantitative spectroscopic study to decipher the fluorescence properties and the multi-step photochromic reaction of DASA compounds. Photokinetic analyses, down to the millisecond range, according to a three-species model, allowed us to characterize the photochromic reaction (quantum yields and kinetic rate constants) involving an intermediate folded open-form, [4] for two different DASA molecules holding different substituents (alkyl or pyrene moieties) on the donor part. To complete the picture, additional information have been collected from combined absorption / fluorescence experiments as a function of irradiation time.

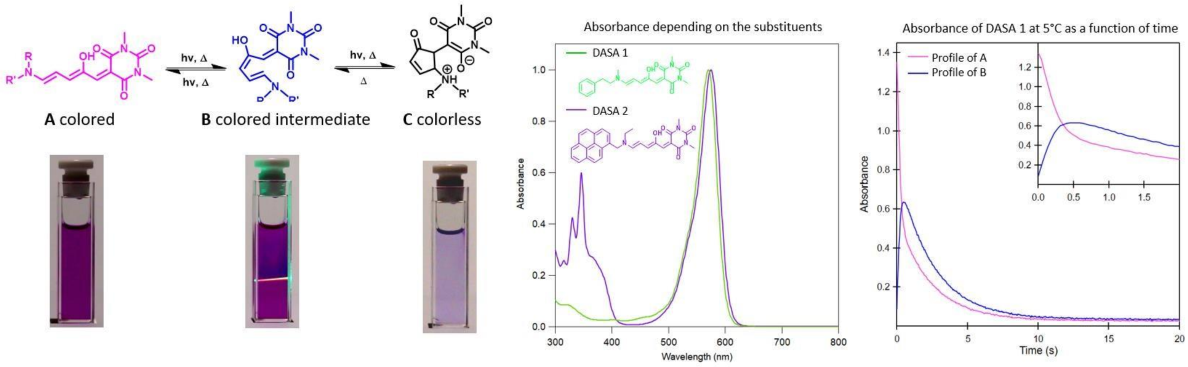

Figure 1. (Left) Photochromic reaction of DASA molecules involving an intermediate folded colored isomer. (Center) Absorption spectra of the two studied molecules. (Right) Photokinetics of A and B forms of DASA 1. Inset : zoom on very short time scale.

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OC3

Luminescence of Pyridines Bearing an Intramolecular Hydrogen Bond

Samuel Guieu[1,2]*, Luís F. B. Fontes[1,2], Cátia I. C. Esteves[1], Raquel Nunes da Silva[1], João Rocha[2], Artur M. S. Silva[1]

[1]LAQV-REQUI*M*TE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]CICECO-Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

* *sguieu@ua.pt*

The dynamic nature of proton transfer and its effect on the photophysical properties of organic dyes is an attractive strategy to create responsive probes and materials. If the dyes have an intramolecular hydrogen bond offering the possibility of tautomerism, their photophysical behaviour may become more difficult to rationalize, and this may impede their applications.[1]

Different series of intramolecularly hydrogen-bonded pyridine dyes have been synthesized and characterized (**Figure 1**). Their structures have been varied using different hydrogen bond donors (phenol[2] and aniline[3]) on a pyridine central core decorated with donor and acceptor substituents, to perceive the influence of each substitution on their photophysical properties. The susceptibility of these moieties to pH variations has also been studied, elucidating that the level of protonation had a significant effect on the emission intensity and colour. The assignment of each emission band was made using DFT and td-DFT calculations, that were in agreement with the experimental results, allowing the rationalization of the emissive processes.

This study emphasizes the versatility of pyridines as organic dyes, which can be synthetized and tuned effortlessly, in order to have the desired proton transfer modulation and subsequent emission response.

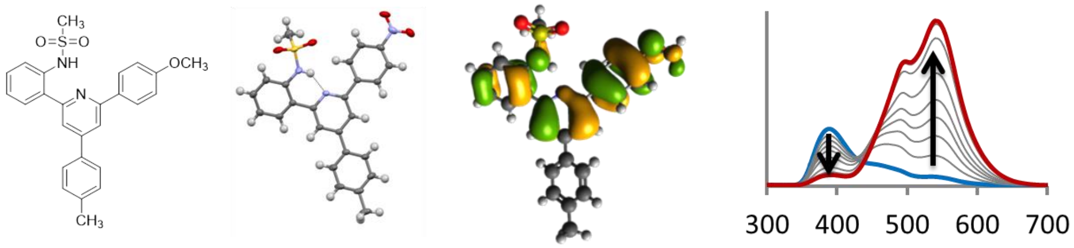

Figure 1. *Illustration of the chemical structure, crystal structure, molecular orbitals and emission spectra of hydrogen bonded pyridine fluorophores.*

Acknowledgements: Thanks are due to University of Aveiro, FCT/MCTES, Centro 2020 and Portugal2020, the COMPETE program, and the European Union (FEDER program) via the financial support to the LAQV-REQUI*M*TE (LA/P/0008/2020 DOI:10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI:10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI:10.54499/UIDB/50006/2020), to the CICECO-Aveiro Institute of Materials (UID/CTM/50011/2019, UIDB/50011/2020 & UIDP/50011/2020), LFBF thanks the FCT for his PhD grant (SFRH/BD/150663/2020).

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OC4

Solar fuels production from Conjugated Porous Polymers: insight into the photochemical pathway

Marta Liras*, Miguel Gomez-Mendoza, Sandra Palenzuela-Rebella, Tania Mazuelo, Teresa Naranjo, Laura Collado, Mariam Barawi and Victor, A. de la Peña O´Shea

**marta.liras@imdea.org*

Artificial photosynthesis (AP) process mimics the nature and comprise hydrogen production, CO_2 photoreduction, and nitrogen fixation processes. In this sense, during the last years our research group has been focused on the study of Conjugated Porous Polymers (CPPs) and Covalent Organic Framework (COFs) and ground-breaking materials for solar fuels production.[1] We have explored the design, advanced characterization, performance and in some cases solar scale-up of hybrid materials composed by CPPs or COFs and TiO_2 as inorganic counterpart.[2] Thus, CPPs or COFs, and hybrid thereof, based on different moieties such as BODIPY,[3,4] BOPHY,[5,6] truxene,[7] phenylene vinylene,[8] thiophene,[9] phenanthrenequinone[10] and so on, has been tested. Derived from these works we have been able to elucidate the charge transfer mechanism between both organic and inorganic counterpart. The combination of spectroscopic techniques such as time -resolve fluorescence and transient absorption spectroscopy (TAS) as well as microscopy techniques such as field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) allow us to determinate if the charge transfer occurs via type II of Z-scheme charge transfer dynamic. Furthermore, we are now able to predict in function the transient lifetime the sort of dynamic and also, the final performance as photocatalyst. Other aspect as nanostructuration of the materials has been studied in line with applications in the photoelectrochemical field.[8,11,12]

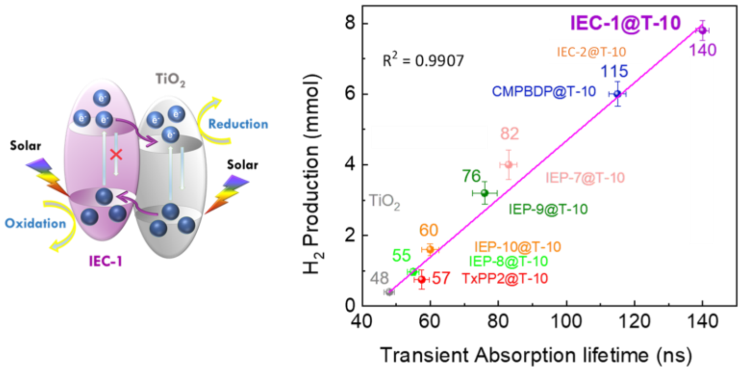

Figure 2. Type II charge transfer mechanism (*left*) and correlation between H_2 production and Transient absorption lifetime of different hybrid materials based on CPPs and COFs (*right*).

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OC5

Helical donor-acceptor Platina[5]helicenes Complexes for Dual Luminescence and Near-infrared Circularly Polarized Luminescence

Maher Hojorat[1]*, Vázquez-Domínguez[2], Abel Ros[2], Denis Jacquemin[3], Ludovic Favereau[1]

[1] Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.
[2] Institue for Chemical Research (CSIC-US), C/Américo Vespucio 49, E-41092 Seville, Spain.
[3] Laboratoire CEISAM, UMR 6230, CNRS, Université de Nantes, Nantes, France.
* *maher.hojorat@univ-rennes.fr*

The design of chiral π-conjugated materials that can manipulate circularly polarized light (CP-light) has recently attracted the attention due to their potential in numerous fields of technology, such as 3D display, sensors, information storage, spintronics, optoelectronic devices as well as in bio-imaging.[1] Historically, chiral lanthanide complexes has been intensively investigated for their high CP luminescence (CPL) intensity with high dissymmetry factor ($g_{lum} = 2(L_L-L_R)/(L_L+L_R)$). Recently, chiral organic and organometallic materials have attracted more attention as CP-light absorbers and emitters due to their superior quantum yields (Φ) and readily tuneable photo-physical and chiro-optical properties.[2]

In this communication, I would like to present our recent results regarding the design of chiral platina[5]helicenes complexes based on donor-acceptor π-conjugated helical ligands. At ambient conditions, these Pt-complexes display far-red and NIR fluorescence and phosphorescence emissions, whose intensity being related to the intrinsic charge transfer character of the helical organic ligand. In addition, these complexes exhibit NIR CPL with considerable dissymmetry factor ($g_{lum} = 1.5 \times 10^{-3}$, Figure 1), affording an interesting molecular design to develop chiral emitters in this low energy region of the spectrum.

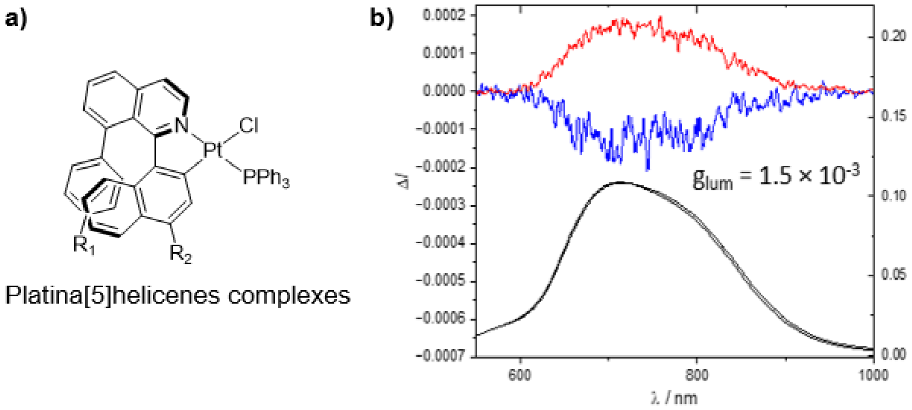

Figure. a) General structure of platina[5]helicenes complexes. b) CPL (top) and luminescence (bottom) spectra with dissymmetry factor value for chiral platina[5]helicenes complexes..

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OC6

Chiral Cr(III) complexes with Bright Circularly Polarised Luminescence

Maxime Poncet,[1] Carlos Moreno Cruz,[2] Sandra Míguez-Lago,[2] Araceli Gonzalez Campaña,[2]
JuanManuel Herrera,[3] Claude Piguet[1] and Juan-Ramón Jiménez*[1,3]

[1] Department of Inorganic and Analytical Chemistry, University of Geneva, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland

[2] Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Granada and Unidad de Excelencia en Química (UEQ), Avda. Fuente Nueva s/n, 18071, Granada, Spain.

[3] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada and Unidad de Excelencia en Química (UEQ), Avda. Fuente Nueva s/n, 18071, Granada, Spain.

jrjimenez@ugr.es

Circularly Polarized Luminescence (CPL) is a matter of study not only because it provides valuable information about the structure of the excited-states in chiral chromophores, but also because it is a powerful tool in the field of bio-applications and material sciences. Generally, promising photoactive emissive chiral materials should fulfill at least: (i) good chemical stability, (ii) large dissymmetry factor (g_{lum}), which quantifies the degree of handedness of a CP emission, and (iii) large absorption and emission properties. Chiral chromophores based on organic molecules and 4d and 5d metal complexes can be straightforwardly prepared but they usually suffer from low g_{lum} because of the strong electric dipole (ED) character of their radiative transitions [1]. Contrary, some f-f transitions can provide large g_{lum} and thus 4f-based metal complexes are currently the best candidates in the field of CPL [2]. However, (i) 4f metals require considerable production costs and (ii) 4f-based metal complexes are usually labile which can make difficult chiral resolutions and subsequent CPL solution studies. Alternatively, chiral complexes based on earth-abundant metals, particularly those incorporating the “inert” Cr(III) ion, benefit from a renewed interest according to their favourable spin-flip luminescence. In this contribution, we will discuss: (i) the state-of-the art in the CPL field (ii) the design principle, chiral resolution and chiroptical properties of a family of Cr(III) complexes as well as their insertion into silica nanoparticles [3, 4, 5]. Finally, we will briefly discuss the on-going efforts for the incorporation of Cr(III) ions in chiral supramolecular structures.

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OC7

Quantum coherent energy transfer in DNA hybrids

Maria João B. Lopes[1,2*], Susana P. G. Costa[2], Jana B. Nieder[1]

[1] INL - International Iberian Nanotechnology Laboratory, Avenida Mestre José Veiga s/n, 4715-330 Braga, Portugal
[2] Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
*maria.lopes@inl.int

The phenomenon of light migration via resonant energy transfer is of fundamental importance in nature. In photosynthetic organisms, light is absorbed and transferred by highly ordered pigment aggregates within specific protein scaffolds located in the light harvesting complexes (LHCs) to achieve highly efficient and ultrafast exciton transport involving localized quantum coherence.[1] J-aggregates are known to present excitonic properties of strongly coupled dye aggregates that often resemble those natural pigments.[2]

The DNA structure, as a programmable scaffold, potentially provides a means for integrating directional energy transfer through templated aggregates with other photonic components that supply or use excitation energy. DNA hybrids have been demonstrated to mediate energy transfer between donor and acceptor molecules attached to either DNA ends, allowing the energy to be transferred from the excited donor dye through a number of identical transmitter dyes to a single acceptor fluorophore.[3,4]

To understand and mimic natural processes of light harvesting, it is key to construct artificial systems that efficiently control light transfer. In this communication, it is presented the excitonic energy transfer properties of synthetized hybrid DNA wires with 30 and 50 base pairs, with selected donor and acceptor fluorophores attached to the termini. We used PIC, a cyanine dye based on a quinoline, whose J-aggregates have been used as energy bridges and transmitter dyes, and the quantum nature of this energy transfer is discussed.

Acknowledgements
This work was supported by the Quantum Portugal Initiative promoted by INL and FCT, through PhD grant SFRH/BD/151096/2021, and FCT for funding through CQUM (UID/QUI/00686/2020. The authors acknowledge access and support from the Nanophotonics and Bioimaging core facilities (NBI) of INL.

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OC8

Understanding the Aggregation Induced Emission (AIE) in a heterocyclic tetraphenylethylene analog

Mathilde Seinfeld[1]*, Jean Rouillon[2], Raphael Rullan[1], Chantal Andraud[1], Tangui Le Bahers[1], Cyrille Monnereau[1]

[1] Laboratoire de Chimie, ENS de Lyon, UMR CNRS 5182, Lyon 69007 France
[2] Department of Chemistry, Chalmers University of Technology, 412 96 Gothenburg, Sweden
* *mathilde.seinfeld@ens-lyon.fr*

While nowadays ubiquitous in a variety of optoelectronic applications, fluorophores displaying emission exclusively in solid state and in particular those constructed around the tetraphenylethylene (TPE) core suffer some limitations. In particular, although it has been reported in many instances[1,2] that the stereoconfiguration around the central double bond may severely impact the solid state luminescence, a stereoselective synthesis of extended TPE cores remains challenging, and separation of diastereoisomer mixtures is generally tedious[3]. Thanks to a stereoselective McMurry coupling[4] followed by a click cycloaddition, we introduce a new chemical group to induce AIE which, although closely related to TPE, can easily be synthesized in a pure (E) configuration with 100% stereoselectivity. Comparison of the spectroscopic properties with the (Z) isomer, obtained by photoisomerization revealed important difference of emission in nanoprecipitate (Φ_E=14% against Φ_z=54%) underlining the importance of the stereochemistry in the AIE properties. Through a combined set of spectroscopic experiments, crystal structure resolution and computational modeling, we also show that the photophysical basis of these AIE properties is due to the flexibility at the excited state around the central C=C bond, allowing fast relaxation to the ground state via a conical intersection.

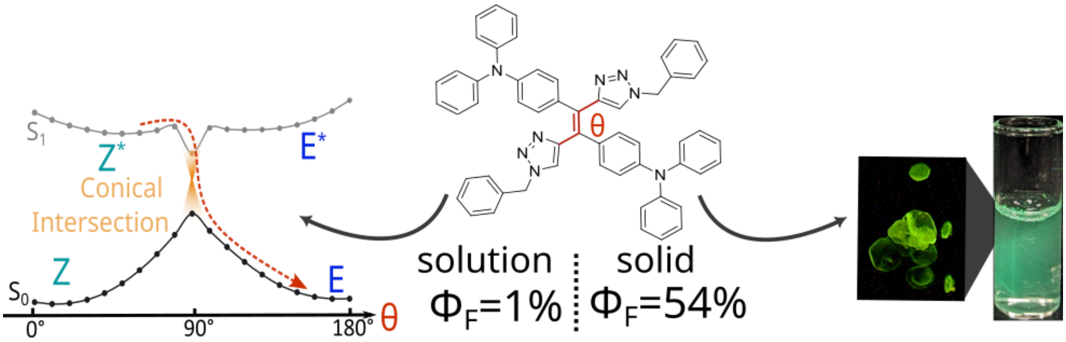

Figure. *Weak fluorescence in solution due to Z/E photoisomerization through rotation around θ at the excited state. Restored fluorescence in aggregates illustrating the AIE properties.*

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OC9

The BASHY Dye Platform: Versatile Fluorophores with Capacity to Photosensitize Singlet Oxygen Formation

Francisco G. Blandón-Cumbreras[1]*, Gilles Gasser[2], Pedro M. P. Gois[3], Uwe Pischel[1]

[1] Center for Research in Sustainable Chemistry (CIQSO), University of Huelva, Huelva E-21071, SPAIN.
[2] Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, Paris F75005, FRANCE.
[3] Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Lisboa 1649-003, PORTUGAL.

* *fcogerman.blandon@ciqso.uhu.es*

Boronic-acid derived salicylidenehydrazone (BASHY) complexes are a new dye platform with interesting application potential in fluorescence bioimaging.[1,2] These dyes are conveniently prepared in a multi-component reaction and can be fine-tuned with regard to their electronic properties, having direct implications for their photophysical behavior.[1] The photophysical properties are governed by the salicylidenehydrazone backbone, which can be designed to control a delicate balance of intramolecular charge-transfer (ICT) and cyanine-like excited-state character.[2] Herein we report the triplet-excited state pathways of purposefully designed BASHY dyes, leading to the photosensitization of singlet oxygen ($^1O_2$) and the use in photodynamic therapy.[3] Furthermore, we designed a dye that can be activated by chemical inputs through chemiluminescent resonance energy transfer. This opens possibilities to form $^1O_2$ in the absence of light excitation. The synthesis, photophysics, and therapeutic application of the devised BASHY dyes will be disclosed in detail.

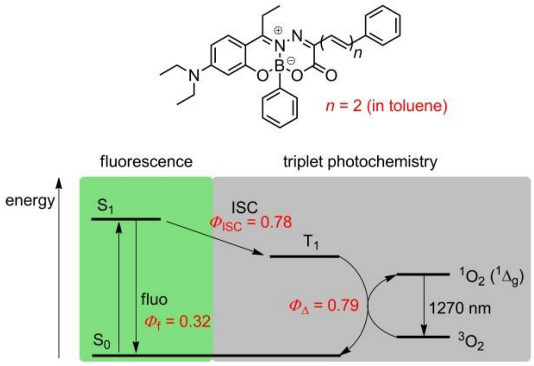

Figure. *The triplet-excited state pathways designed for BASHY, leading to singlet oxygen sensitization.*

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OC10

Photophysics and thermally activated delayed fluorescence (TADF) of fullerene C70 and C70 methano and pseudodihydro monoadducts: A comparative study.

Tiago Palmeira* and Mário N. Berberan-Santos

iBB – Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal
* tiago.palmeira@tecnico.ulisboa.pt

Fullerenes, particularly C60 and C70, garnered significant interest due to their unique structure and distinctive physical and chemical properties, including their photophysics. Functionalizing C60 and C70 by attaching various functional groups to their cage-like structures provides a versatile means to create a wide variety of electroactive systems and fine-tune their optical properties for different applications, which include solar cells, rechargeable batteries, and biomedicine[1-3].

This study presents a comparative analysis of the photophysical properties of pristine C70 and two of its derivatives, a methano adduct (MC70, also known as PC71BM) and a pseudo-dihydro adduct (DC70), focusing particularly on their thermally activated delayed fluorescence (TADF)[4-7]. The primary objective is to understand how the photophysics and, consequently, the singlet and triplet decay rate constants are affected by the monoderivatization of C70, the bonding being by one (MC70) or two (DC70) carbon atoms.

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OC11

Dual emission in triphenylamine decorated anthracenes

José Santos[1]*, Lucy A. Weatherhill[2], Diego J. Vicent[1], Paloma L. dos Santos[3], Fernando B. Dias[2], Nazario Martin[1]

[1] Departamento de Química Orgánica, Universidad Complutense de Madrid (Spain)

[2] Physics Department, Durham University (UK)

[3] Department of Electronic and Electrical Engineering, University of Sheffield (UK)

**jsantosb@ucm.es*

Light emission in organic molecules must always originate from relaxation from the lowest energy excited state of a given multiplicity, either singlet (S_1) for fluorescence or triplet (T_1) for phosphorescence [1]. This assertion is known as Kasha's rule and is generally followed by most known molecules. As with almost every rule, there are always exceptions, like the archetypical azulene[2] which emits from its S_2 level, or molecules capable of simultaneously emitting from two states. The latter known as dual emission [3,4], has recently become more common as research on thermally activated delayed fluorescence (TADF) design molecules with close in energy states. In these molecules Kasha's rule is neglected due to the spatial separation of the states, which allows the competition between internal conversion to S_1 and fluorescence from S_2.
Herein, we present the synthesis of a series of emitters based on different anthracene cores decorated with triphenylamines. Interestingly, all systems show dual emission in solution and a strong solvatochromic effect. Emission in films evidences remarkable red-shifts with high PLQYs at low concentration, although sharp drop is observed upon concentration. Our findings, suggest that emitters with strong red emission are possible if aggregation caused quenching is prevented.

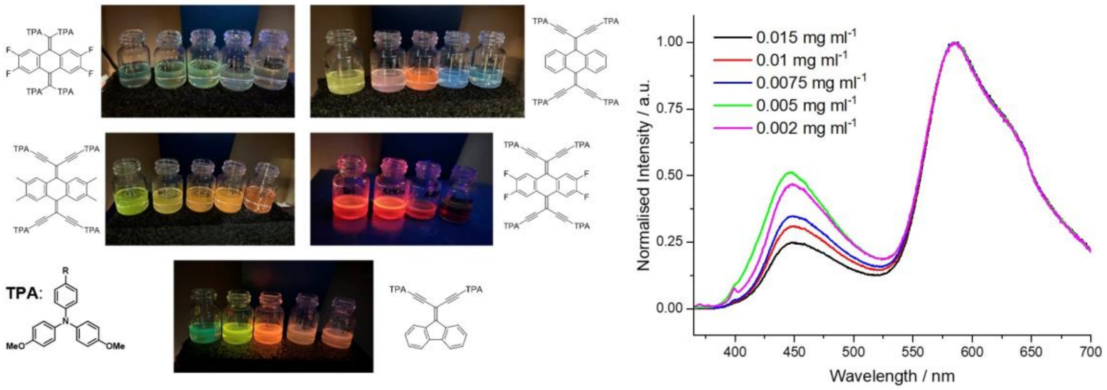

Figure. *Molecular structure of the emitters and emission of samples in solutions of varying polarity upon excitation with a 365 nm lamp.*

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OC12

Excited-stated engineering: harnessing lanthanide ions as energy reservoirs

Anh Thy Bui[1]*, Charles Ciambrone[1], Clotilde Davies[1]

[1]Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France

anh-thy.bui@u-bordeaux.fr

Rare earth-containing materials are ubiquitous in diverse applications, luminescence-based purposes accounting for about a third of their uses.[1] The search for structures with optimal properties for detection, sensing or lighting for instance, has led to general design rules to optimize luminescence emission in lanthanide complexes, taking advantage of their spectrally sharp and long-lived metal-centered emission.[1,2] In this contribution, we will discuss situations where the complex can undergo reverse energy transfers to an organic chromophore,[3] a scenario that is usually undesired due to its efficiency in deactivating the lanthanide core. By tackling the problem from the organic dye standpoint, we will evidence unusual and intriguing photophysical behaviors that could lead to new families of TADF (thermally activated delayed fluorescence)[4] emitters.

Figure. *Left: schematic representation of a lanthanide complex.*
Right: pictures of luminescent powders of TADF dyes under 365 nm irradiation.

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OC13

Immobilised Bi-Halide Perovskite for Oxidative Photocatalytic Coupling of Benzyl Alcohol and Benzylamine

Joana C. Lopes[1,2]*, Manuel Peñas Garzón[1,2], Maria J. Sampaio[1,2], Cláudia G. Silva[1,2], Joaquim L. Faria[1,2]

[1]LSRE-LCM – Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr Roberto Frias, 4200-465 Porto, Portugal
[2]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr Roberto Frias, 4200-465 Porto, Portugal
* *joanacl@fe.up.pt*

Traditional methods for imine synthesis involve the condensation of amines with aldehydes or ketones using dehydrating agents and homogeneous catalysts, often resulting in by-products and requiring high temperatures and pure oxygen. Recently, the cross-coupling of primary amines with alcohols has gained attention for being atom-efficient and environmentally friendly, producing less waste. Heterogeneous photocatalysis has shown significant potential in imine synthesis, though controlling selectivity remains challenging. Thus, designing effective photocatalysts and precisely controlling reaction conditions are crucial for practical applications. Halide perovskites are known for their optoelectronic properties, but the most efficient ones contain lead, causing environmental concerns. Bismuth-based perovskites have emerged as promising photocatalyst alternatives due to their narrow bandgap and high surface area, providing a high density of active sites. Combining continuous operation with immobilised photocatalysts improves productivity, reduces resource consumption, and enables seamless scale-up to industrial levels.

In this work, caesium bismuth bromide perovskites ($Cs_3Bi_2Br_9$, CBB) were synthesised by a one-step solution process and employed to produce N-benzylidenebenzylamine (BZI) under visible light radiation at ambient conditions. Immobilising CBB in a 3D-PET structure enables efficient BZI production without a final catalyst separation step. The photocatalytic evaluation demonstrated that supported CBB allowed the complete conversion of benzylamine and benzyl alcohol after 1 h, yielding 70 % of BZI in basic medium operating in batch mode. Continuous production of BZI was successfully achieved using immobilised CBB, with a maximum yield of 0.35 mM of BZI after 2 h reaction, and the supported CBB remained stable after more than 50 h reaction.

Acknowledgements: This work was financially supported by the national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI:10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020), by SuN2Fuel (2022.04682.PTDC), funded by national funds through FCT/MCTES (PIDDAC). JCL acknowledges the PhD research grant from FCT, Ref. 2020.04651.BD (DOI: 10.54499/2020.04651.BD). Manuel Peñas-Garzón acknowledges his postdoctoral fellowship from Fundación Ramón Areces (XXXIV Convocatoria Ciencias de la Vida y de la Materia). MJS acknowledges FCT funding under the Scientific Employment Stimulus - Institutional Call (CEECINST/00010/2021/CP1770/CT0011).

OC14

Two-photon absorbing Ir(III) complexes as sensitizers for a new generation of brighter and color tunable emissive lanthanide nanoparticles

Juan Manuel Herrera[1]*

[1]Departament of Inorganic Chemistry, Faculty of Sciences, University of Granada. Avda. Fuentenueva s/n, 18071, Granada, Spain

* *jmherrera@ugr.es*

Currently, fluoride-based lanthanide nanoparticles (LnNPs) are at the forefront of lanthanide luminescence and related applications (lighting, security inks, bioimaging, etc.).[1] These materials exhibit excellent photostability, tunable color emission depending on the optically active lanthanide dopants, and very long-lived emissions. Hovewer, due to their intrinsically high surface-to-volume ratio, their emissions are severely quenched by surface defects. Furthermore, the very narrow and low absorption of the forbidden f-f transition bands requires the use of high intensity excitation sources at very limited excitation wavelengths.[1]

Recently, we have demonstrated the ability of a blue-luminescent Ir(III) chromophore to sensitize Eu(III)-emission from Eu-doped LaF_3 particles via Ir → Eu energy transfer. Compared to bare LaF_3:Eu particles, the hybrid composite LaF_3:Eu@Ir exhibits a brighter luminescence and its color emission can be regulated by selective excitation of the Ir(III) or Eu(III) centers. In addition, the Ir(III) moiety can be excited by either UV-Vis/NIR light through one-/two-photon absorption processes.[2]

In this communication, the latest results of our group in the search for ultrabright and color tunable composites based on LnNPs and Ir(III) complexes as sensitizers are presented.

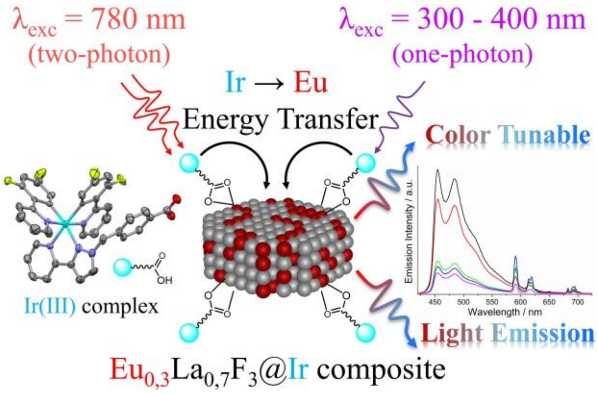

Figure. *Schematic representation of LaF_3 :Eu@Ir composite showing color tunable emission sensitized by Ir → Eu energy transfer.*[2]

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OC15

9-Borafluoren-9-yl and diphenylboron tetracoordinate complexes of 8-quinolinolato ligands with heavy-atoms substituents: synthesis, fluorescence and application in OLED devices

Carina B. Fialho[1]*, Tiago F. C. Cruz [1], Maria José Calhorda[2], Luís F. Vieira Ferreira[3], Piotr Pander[4], Fernando B. Dias[4], Pedro T. Gomes[1]

[1] Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
[2] BioISI - Instituto de Biossistemas e Ciências Integrativas, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
[3] BSIRG – Biospectroscopy and Interfaces Research Group, IBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal.
[4] Department of Physics, Durham University, South Road, Durham DH1 3LE, U.K.

* *carinafialho@hotmail.com*

In Organic Light-Emitting Diode (OLED) devices, it is crucial to utilise all excitons generated by electrical excitation, which produce 25% of singlet states and 75% of triplet states. Therefore, an effective utilisation of triplet states is essential to enhance devices efficiency. Up-conversion mechanisms such as Triplet-Triplet Annihilation (TTA) and Thermally Activated Delayed Fluorescence (TADF) are widely employed to harvest the dark triplet states. The TADF process largely depends on the energy difference between the singlet and triplet states (ΔE_{ST}), which can be minimised by reducing the overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the emitting molecule, the Boron atom being extensively used as a hub to anchor the two orbitals, preventing their overlap.[1,2] In this study, we report the synthesis and photophysical characterisation, including steady-state and time-resolved studies, of new tetrahedral boron complexes. These complexes feature an 8-quinolinolato chelating ligand substituted with Br or I atoms, linked to 9-borafluoren-9-yl or diphenylboron fragments. Delayed fluorescence (DF) was observed, and studies on the DF mechanism were conducted. Among the synthesised compounds, those suitable for application in OLEDs were employed as emitters in OLED devices.[3]

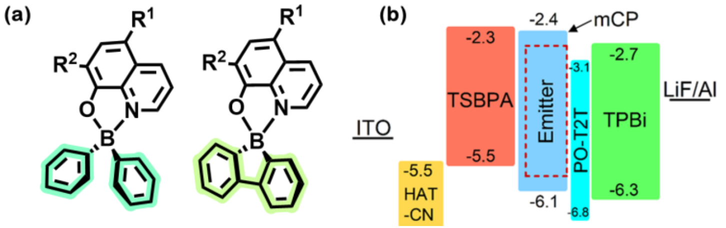

Figure. *(a) Tetrahedral boron complexes studied. (b) Graphical representation of the OLEDs architecture.*

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OC16

Nanometrology based control: Taming surface photografting with attoL precision

Baptiste Maillot[1], Jean Frédéric Audibert[1], Fabien Miomandre[1], Clément Lafargue[2], Pascal Berto[3],
Vitor Brasiliense[1]*

[1]Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, 4 av. des sciences, 91190 Gif-sur-Yvette, France
[2]Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, 4 av. des sciences, 91190 Gif-sur-Yvette, France
[3] Sorbonne Université, INSERM, CNRS, Institut de la Vision, Paris, F-75012 France

* *vitor.brasiliense@ens-paris-saclay.fr*

Strategies for local and controlled surface modification with organic groups are often hampered by the lack of in situ methodologies to measure the extent of surface modification reactions. Indeed, factors such as inhomogeneous surface conditions, vibrations, intensity fluctuation lead to uneven surface modification rates and high surface to surface dispersion. Chemical strategies for control of the radical process exist (ALD, RAFT, etc.), they are often restrictive in terms of implementation conditions or of the chemical groups that can be added.

In this work, we introduce an alternative approach to local surface modification control, based on operando optical nanometrology [1]. Taking photochemically generated aryl radical molecules as prototypical examples of uncontrolled aqueous surface modification reactions, we first demonstrate that QPI enables mechanistic analysis of surface photochemical microfabrication reactions since their onset [2]. The strategy is flexible and can be used in many configurations, as we show here in direct laser writing and stereolithography inspired microfabrication. We demonstrate that, in spite of surface modification kinetics spanning four orders of magnitude, precise surface modification can be achieved (attoL precision) [3]

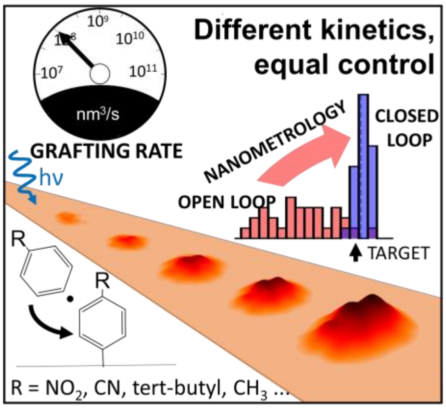

Figure. *Principle of nanometrology based control applied to surface modification with photogenerated radicals.*

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OC17

Ultrafast dynamics of push-pull dyes for near-IR transparent Dye-Sensitized Solar Cells

Simon Ali Rincon Celis[1], Ilias Nikolinakos[1], Thibaut Baron[2] , Yann Pellegrin[2], Frédéric Sauvage[3],
Fabrice Odobel[2], and Stefan Haacke[1]*

[1]Université de Strasbourg, Institut de Physique et de Chimie des Matériaux Strasbourg, UMR 7504, France
[2]Chimie et Interdisciplinarité : Synthèse, Analyse, Modélisation, UMR 6230, Université de Nantes, France
[3]Lab. de Réactivité et Chimie des Solides, UMR 7314, Université de Picardie Jules Verne, Amiens, France

*stefan.haacke@ipcms.unistra.fr

When it comes to integrating solar cells in buildings, transparent and colorless solar cells have been actively explored in the past decade.[1] Dye-sensitized solar cells are an appealing solution in this context since the absorption properties of dyes can be tuned to be selective in the near-IR and UV range. To this end, we have recently introduced the near-IR cyanine-based sensitizers VG20 and TB207, which present high extinction coefficients (≈$1.3x10^5$ M^{-1} cm^{-1}), and power conversion efficiencies (PCE) of 3.1 and 3.85 %, respectively, as well as average visible transmissions comparable to those of commercial windows.[2,3] Here, we report on the two novel near-IR absorbing pyrrolopyrrole cyanine-based dyes TB336 and TB423 (Figure 1), which bear a so-called "Hagfeldt donor group" that introduces a push-pull electron character reducing the charge recombination and possibly fostering electron injection.[4] The former dye absorbs maximally at 764 nm (ε~128,000 $M^{-1}cm^{-1}$) and the latter at 757 nm (ε~134,000 $M^{-1}cm^{-1}$) in solution. TB423 shows a PCE of 3.85% while TB336 reaches 4.1% (unpublished), making it the most promising near-IR dye in terms of DSSC performance. We investigated DSSCs made with these dyes via fs-transient absorption (TAS) and fluorescence up-conversion spectroscopy (FLUPS) to assess the competition of carrier injection and resonant energy transfer due to aggregates.

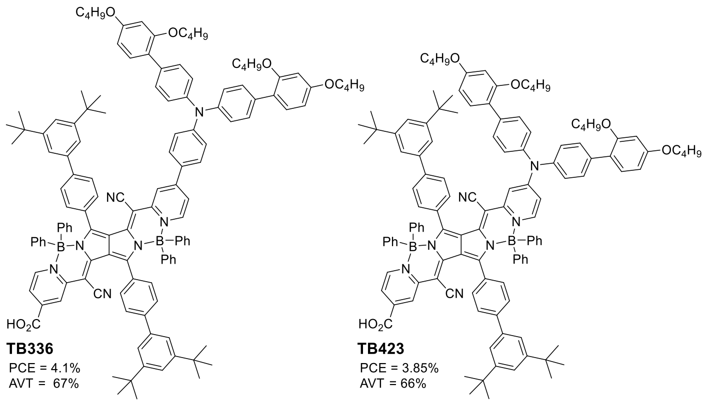

Figure 1. *Chemical structure of the photo-sensitizer TB336 and TB423.*

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OC18

Chromoionophores for Li-ion battery electrolyte leakage detection

Ricardo da Costa Barata[1]*, Fabio Ferrario[1], Natalia Lebedeva[1]

[1] *European Commission, Joint Research Centre (JRC), Petten, The Netherlands*
**ricardo.da-costa-barata@ec.europa.eu*

The wide deployment of batteries is a key aspect of the transition to climate neutrality. While they are already a part of our daily lives, from small uses such as laptops to larger such as electric vehicles, the demand for sustainable batteries is likely to increase in the coming years[1].

Li-ion batteries have become the dominant battery technology for many applications such as electromobility, stationary energy storage and portable (consumer) electronics [2]. The safety risks associated with a possible release of electrolytes and their degradation products from contemporary Li-ion batteries [3] introduce the need for a reliable and robust method for detection of such a release.

In the current regulatory framework [4], “visual inspection without disassembling any part of the TestedDevice” is used as a verification method for electrolyte leakage and venting. This method however poses limitations. On the one hand, it may not always yield consistent results due to e.g. high volatility of the electrolyte solvents; on the other hand, it does not allow distinguishing between battery coolant leakage and electrolyte leakage [2].

In the current work, we explore the use of chemical compounds that visually signal the presence of Li ions after selectively reacting with Li ions and not with other components of the electrolyte and/or coolant. We explore both fluorescence- and colour-changing compounds. Such compounds can also help to differentiate between electrolyte and coolant leaks, thus improving the specificity of the detection method.

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OC19

Deciphering surface interactions of microcrystals found in osteoarthritic joint by staining with fluorescent organic nanoparticles

Maxime Munch[1], Florentin Chauveau[1], Eléna Ishow[1]*, Louize Touati[2], Stéphane Sarda[2], Christèle Combes[2], Charles Leroy[3], Hang-Korng Ea[3], Etienne Laborde[4], Chantal Damia[4]

[1]Nantes Université, CNRS, CEISAM, UMR 6230, F-44000 Nantes, France
[2]Toulouse INP, CNRS, CIRIMAT, UMR 5085, F-31030 Toulouse, France
[3]Hôpital Lariboisière, INSERM, BIOSCAR, U1132, F-75010 Paris, France
[4]Centre Européen de la Céramique, CNRS, IRCER, UMR 7315, F-87068 Limoges, France

**elena.ishow@univ-nantes.fr*

Osteoarthritis is a strongly disabling and painful disease, resulting from the progressive destruction of cartilage cells in joints, and currently facing the absence of curative treatment. Recent studies have showed that cartilage calcification, stemming from the accumulation of calcium orthophosphate (apatite) and calcium pyrophosphate microcrystals, is associated to strong degradation of the patient's state.[1] Hence, knowing about the biological fate of these crystals and their interactions with cells is of utmost importance. The most common bioimaging technique relies on computerized tomography involving X-ray absorption, which is little adapted to dynamic follow-up. By contrast, fluorescence optical microscopy allows for high spatial resolution, *in cellulo* investigations and high sensitivity, which however requires fluorescent labelling of the crystals. Whereas several dyes, especially fluorescent ones, have been reported to efficiently stain apatite through calcium interactions,[2,3] calcium pyrophosphate crystals, known to induce strong inflammation, failed to be labelled. In these studies, we want to report on the synthesis of novel amphiphilic red-emitting fluorophores amenable to self-assemblies as fluorescent organic nanoparticles in water[4] and efficient staining of both kinds of crystals, issued from controlled synthesis (Figure 1). By tuning the chemical composition of the fluorophores, differentiate crystal staining is evidenced through time-resolved and steady-state emission measurements, revealing distinct surface interactions through water and ion exchanges. Spectral fluorescence microscopy of single crystals evidences similar energy of the emission bands, whatever the location, suggesting close electronic surroundings and homogenous interactions upon cell internalization.

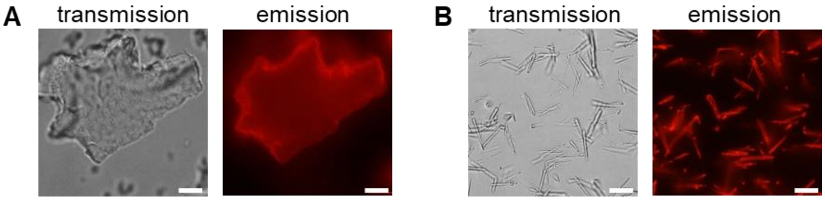

Figure 1. *Transmission and fluorescence microscopy before and after staining with fluorophores of: A) calcium phosphate crystals, B) calcium pyrophosphate crystals (scale bar: 10 µm).*

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OC20

Metal-Organic Frameworks in Lighting Applications

Cristina Martín,[1] Víctor Rubio-Giménez,[2] Johan Hofkens,[3] Rob Ameloot [2]

[1] Departamento de Química Física, Facultad de Farmacia, Universidad de Castilla-La Mancha, 02071, Albacete, Spain

[2] *Instituto de Ciencia Molecular (ICMol), Universitat de València, Catedràtic José Beltrán, 2, 46980 Paterna (Spain)*

[3] Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy (cMACS), KU Leuven, 3001 Heverlee, Belgium

[4] Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, 3001 Heverlee, Belgium

The current mismatch between energy demand and production levels has spurred the search for new materials to replace the toxic and scarce conventional materials used in lighting. Among the myriad possibilities, Luminescent Metal-Organic Frameworks (LMOFs), with their unique ability to modulate properties by changing the building blocks of their structure, stand out as a beacon of hope.[1].

The use of LMOFs in lighting applications can be tackled by two approaches: i) as down-light converters by coating the outside of blue light-emitting devices (LEDs) or ii) implementing them as an electroactive material in the electroluminescent LEDs [2]. The selection of each approach is based on the characteristics of the specific materials; for example, if the first application is selected, the LMOFs should be stable under continuous UV light irradiation; however, in the case of LEDs, the charge transport properties will be more important in order to get stable devices.

Building on this, our investigation focused on the potential use of various nanostructured LMOFs materials as down converters or light-emitting materials (EM). A comprehensive spectroscopic characterization, employing a range of time-resolved tools, was instrumental in optimizing the lighting device by decoding its photo- and electrical behaviour.

The obtained results not only provide new insights into promising LMOF materials but also set the base for constructing new types of easy, tuneable, hybrid, and cost-effective LEDs.

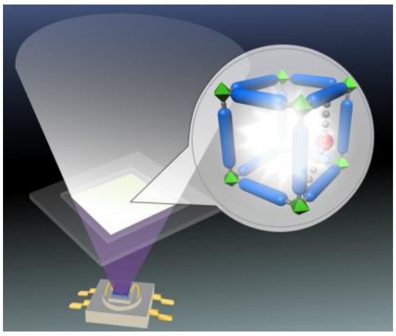

Figure 1. Schematic representation of the work principle of LMOFs in LEDs.

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OC21

Efficient Photocatalyst-Free Formation of C(sp^2)–B(S) Bonds Using Visible Light

Raúl Pérez-Ruiz*

Departamento de Química, Universitat Politècnica de València, Camino de Vera S/N, 46022, Valencia, Spain
* *raupreru@upv.es*

We have witnessed during the last 15 years the great evolution that visible-light photoredox catalysis has experienced as a powerful tool in organic synthesis and formation of new compounds can be now tackle. In this context, generation of radical intermediates such as aryl radicals and their subsequent trapping by the appropriate nucleophile is nowadays one of the main strategies to obtain added-value products.[1] The use of mild conditions and "sometimes" metal-free photocatalysts encompasses this methodology into the green principles from an economical and environmental point of view. Organoboron compounds, environmentally benign scaffolds, attract considerable interest not only in organic synthesis (they can be easily transformed into any other functional group) but also in other scientific areas of research, for example, as conjugated materials such as organic electronic applications and LEDs manufacturing or antimicrobial agents in medicinal chemistry.[2] On the other hand, organosulfur compounds have a key role in nature, and development of new strategies for C–S bonds formation is crucial not only in numerous organic reactions, but also in drug discovery.[3] This is particularly relevant in the synthesis of aryl sulfides, which are significant structural moieties. Moreover, C−S bonds are present in drugs employed for the treatment of different diseases, such as cancer, HIV, and Alzheimer's malady.[4]

Therefore, exploration of new procedures for their construction under milder conditions appears to be a challenge task. The question then arises whether production of new forming C(sp^2)–heteroatom (B, S) bonds can be achieved by visible light as energy source. Herein, we wish to show our recent results on the borylation and thiolation of five-membered heteroarene halides.[5] Interestingly, the corresponding syntheses have followed a photocatalyst-free protocol. In the case of new boronic esters, an easy-to-use gel nanoreactor has been used which has permitted to enhance the production rate and to protect against oxygen poisoning. Regarding the new thioethers, a straightforward methodology involving an EDA complex formation has been successfully employed.

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OC22

Development of Waste-Based Carbon Dots for the Photocatalytic Degradation of Organic Dyes

Luís Pinto da Silva[1]*, Ricardo Sendão[1], Joaquim C.G. Esteves da Silva[1]

[1]Centro de Investigação em Química (CIQUP), Instituto de Ciências Moleculares (IMS), Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.

* *luis.silva@fc.up.pt*

Carbon Dots (CDs) are carbon-based nanomaterials with a quasi-spherical shape, with sizes typically below 10 nm.[1,2] They possess either a nano-crystalline or amorphous core and a surface composed of different functional groups (as amines, carboxylic acids, and hydroxyl groups), which can be tuned by varying the precursors and employed synthesis strategies.[3]

CDs have been attracting much attention from the research community due to their photoluminescence, good water solubility, biocompatibility, low toxicity, (photo)chemical stability, and ease of functionalization.[1,2] Furthermore, they show potential for mass production via green bottom-up procedures and for using organic residues as precursors.[4,5] Thus, it is not surprising that they have been investigated in various applications, including photocatalysis, sensing, bioimaging, and light-emitting devices.[1-4]

Herein, we aimed to develop novel CDs to be employed in the photocatalytic degradation of organic dyes in water under visible light irradiation,[5,6] which is relevant for treating industrial textile wastewater. More specifically, we have produced these CDs from a relevant and ubiquitous agricultural waste, corn stover, allowing for waste upcycling in a circular economy approach. These CDs were then coupled with TiO_2 nanoparticles to form photocatalytic nanocomposites, which were thoroughly characterized by SEM, XPS, XRD, FTIR, NMR, UV-Vis, and fluorescence spectroscopy. The coupling of CDs with TiO_2 enhances visible light absorption and hinders the recombination of photogenerated charge carriers, which enhances the resulting photocatalytic activity. In fact, the resulting nanocomposites showed increased photocatalytic degradation toward organic dyes in water under visible light irradiation, up to ~370% higher than bare TiO_2 nanoparticles.

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OC23

Toward the rational design of tricarbonylrhenium(I) complexes with original solid-state emission properties

Stéphen Le Garrec[1], Valentine Guilbaud[1], Abanoub Mosaad Abdallah[1,2], Corinne Vanucci-Bacqué[1], Florence Bedos-Belval[1], Eric Benoist[1], Suzanne Fery-Forgues*[1],

[1] Université de Toulouse III, Lab. SPCMIB, CNRS UMR 5068, 31062 Toulouse, France.

[2] Narcotic Dept., National Center for Social & Criminological Research (NCSCR), Giza 11561, Egypt.

* *suzanne.fery-forgues@univ-tlse3.fr*

For a long time, tricarbonylrhenium(I) complexes have attracted significant attention due to their stability, very low toxicity and attractive spectroscopic properties, which made them popular bioimaging agents and sensors in solutions.[1] Over the past few years, our team has developed original complexes with promising applications in the field of photoluminescent materials (Fig. 1). They are generally weakly phosphorescent in solution, but exhibit spectacular solid-state luminescence enhancement (SLE).[2-4] Applications of their aggregation-induced emission (AIE) behavior for the detection of biological molecules were envisaged. Additionally, some complexes show unprecedented mechanoresponsive luminescence (MRL) properties, positioning them as good candidates for friction sensing.[5] Recently, binuclear rhenium(I) complexes have also been investigated: the connection between the two rhenium centers influences the molecular geometryand intermolecular interactions, which govern the solid-state emission properties. In the present study, several series of original rhenium(I) complexes were compared, differing by their bidentate organic ligand, ancillary ligand, and number of metal centers. The goal was to identify the structural criteria associated with superior SLE and MLR properties, in order to design rationally a new generation of photoluminescent complexes.

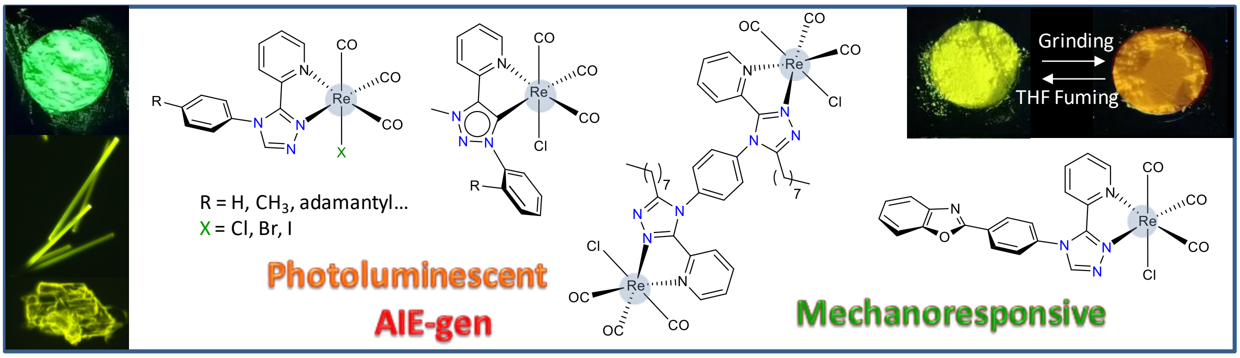

Figure 1. *Some examples of photoluminescent tricarbonylrhenium(I) complexes investigated in this work*

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OC24

Dual-Targeted-BODIPY photosensitizer for Photodynamic Therapy

Jose Luis Chiara[1*],Ruth Prieto-Montero[2], Larissa Maierhofer[1], María D. Chiara[3], and Virginia Martinez-Martinez[2]

[1]Instituto de Química Orgánica General (IQOG-CSIC), Madrid, Spain
[2]Departamento de Química Física, Universidad del País Vasco-EHU, Bilbao, Spain
[3]Instituto de Investigación Sanitaria del Principado de Asturias, Universidad de Oviedo, Hospital Universitario Central de Asturias, Oviedo, Spain.

* *jl.chiara@csic.es*

BODIPY-family dyes are widely known as fluorophores due to their excellent photophysical properties: high absorption coefficient, high thermo- and photostability, and high fluorescence quantum yield. Moreover, BODIPYs have demonstrated a high chemical versatility allowing exhaustive and selective modification to modulate the final photophysical properties. In this sense, the original BODIPY dye could be functionalized and adjusted to achieve efficient BODIPY-photosensitizers; a molecule with high singlet oxygen ($^1O_2$) production able to destroy nearby cells or microorganisms under irradiation and with important applications in photodynamic therapy (PDT). Besides, the anchorage of biotarget to the BODIPY structure will also enhance their selectivity for cells, microorganisms, or organelles. As a result, BODIPY could be exploited in bioimaging (diagnosis) or photodynamic therapy (treatment).[1]

Our group has previously designed a specific mitotracker BODIPY by the addition of L-carnitine moiety to its core.[2] In this work, a dual-targeted PS (mitochondria and lysosomes) is reached by the extra addition of halogen atoms, particularly bromide, to the previously L-carnitine-BODIPY, reaching a good balance between fluorescence and singlet oxygen generation abilities, Figure 1. *In vitro* experiments were carried out in human larynx squamous cell carcinoma to demonstrate their specific accumulation, low cytotoxicity under dark conditions, and phototoxicity activity under specific irradiation.

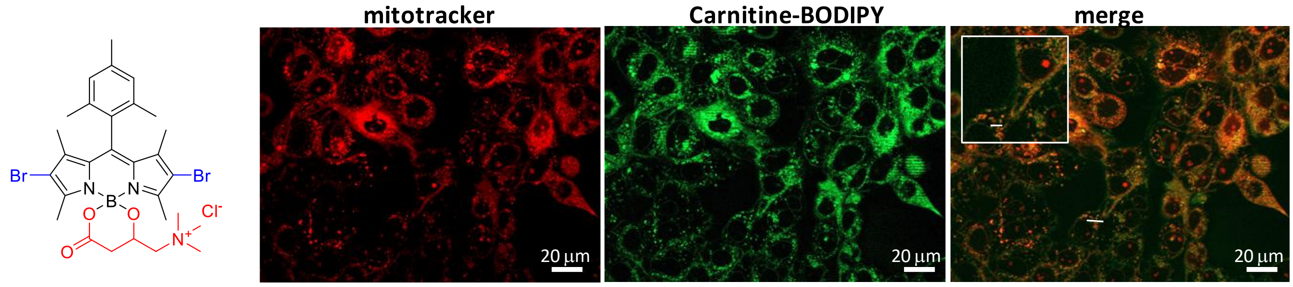

Figure 1. *SCC38 cells treated with Carnitine-BODIPY (green) and MitoTracker Red CMXRos (red) for 30 min. Scale bar 20 µm*

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OC25

Fading memories: The impact of photosensitive eosin lakes on the conservation of 19th-century hand-painted magic lantern slides

Vanessa Otero[1,2,*], Sofia Pires[2], Márcia Vieira[1], João Pedro Veiga[2,3], Ângela Santos[2], Márcia Vilarigues[2]

[1]Department of Conservation and Restoration and LAQV-REQUIMTE research unit, NOVA School of Sciences and Technology (FCT NOVA), Caparica, Portugal
[2]Department of Conservation and Restoration and VICARTE research unit, *ibidem*
[3]Department of Conservation and Restoration and CENIMAT research unit, *ibidem*
* *van_otero@fct.unl.pt*

Magic lantern was a groundbreaking invention that allowed the projection of moving images accompanied by sound and music. It was used all over the world and was a major form of entertainment for collective audiences. The MAGICA project is currently exploring the art of painting glass slides for magic lanterns and how they were used in science academies and entertainment venues in 19th-century Portugal.[1]

This work investigates the red colours of hand-painted magic lantern glass slides belonging to the Portuguese Cinematheque – Museum of Cinema (CPMC). The colours of a particular set have significantly faded, completely altering the original perception of the object (Figure 1). A multi-analytical approach using Energy-Dispersive X-ray Fluorescence Spectrometry, UV-VIS, Raman and micro-Fourier Transform Infrared Spectroscopies identified the presence of eosin complexed with aluminium (Al) and lead (Pb). These early synthetic colourants are known for their high photosensitivity.[2]

For this study, pigments were prepared using eosin Y and different ratios of the complexing agents Al^{3+} and Pb^{2+}.[3] Furthermore, they were applied in glass slides using a mastic binder, commonly identified in historical magic lantern glass slides. To assess the photostability of the paints, these were irradiated with a Xenon lamp ($\lambda_{irr} > 300$ nm) and the degradation process was followed by the above mentioned techniques and further analysed by Wavelength-Dispersive X-ray Fluorescence Spectrometry and High-Performance Liquid Chromatography-Diode Array Detector. This methodology will allow us to improve the accurate identification of eosin lakes in historical magic lantern glass slides and determine the specificities of the pigment formulations that are more prone to degradation.

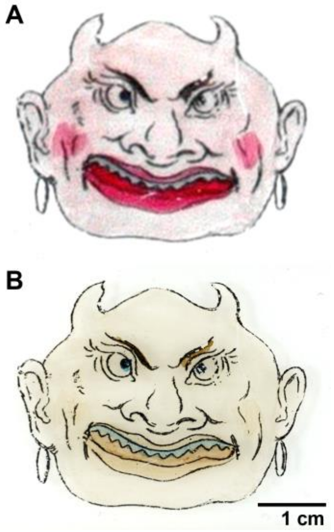

Figure 1. *Detail of the hand-painted magic lantern glass slide CPMC-PC0020/007, **A)** before and **B)** after fading. © CPMC.*

This work will enhance our understanding of the original appearance and conservation condition of eosin reds in historical slides, contributing valuable knowledge to the study and preservation of these detailed heritage objects found in collections worldwide.

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OC26

Modelling the sources of broadening in UV-Vis spectra of organic dyes: from the gas to the crystalline phase

Maxime HODEE[1]*, Daniel ESCUDERO[1]

[1]Computational Photochemistry group, KU Leuven, Leuven, Belgium

* *maxime.hodee@kuleuven.be*

In recent decades, organic dyes have received considerable attention due to their numerous applications, including, but not limited to, organic light-emitting diodes (OLEDs) and Organic Photovoltaics (OPV). Additionally, their chemical diversity, ease of chemical tuning and potential low toxicity, arising from their inherent organic nature, have made them optimal choices for such applications.

While extensive experimental studies have been conducted on the photophysical properties of such systems, theoretical calculations often do not provide a detailed description of the excited state mechanisms. This is due to the limitations of the most commonly used electronic structure methods, which are often restricted to a "vertical" description of photophysical processes. Consequently, there is a lack of information on properties such as peak broadening in absorption/emission spectra and excited state decay processes.

This contribution addresses these limitations. The theoretical methodologies applied to molecular organic materials (such as BODIPYs) are explored, including the vibronic contribution to UV-vis spectra and excited state decay rates in the gas phase, coupled to TD-DFT and wavefunction-based schemes.[1] Then, we expand the discussion to the crystalline phase, assessing different methodologies to estimate the various sources of broadening observed in the crystalline-based UV-Vis spectra. These sources can originate from either static disorder, excitonic coupling and/or vibronic contributions. As a preliminary approach, a QM/MM electrostatic embedding scheme is employed to simulate static disorder,[2] while non-local TD-DFT methodologies are used to estimate excitonic coupling.

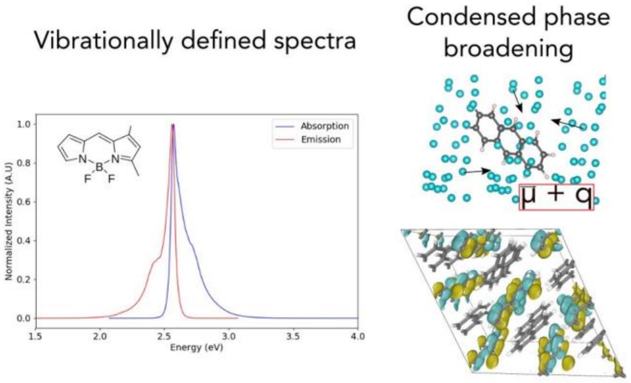

Figure. *Applications of methodologies permitting a non-vertical description of the photophysical properties.*

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OC27

A new generation of smart windows for solar heating control

Marc Villabona[1]*, Jaume Ramon Otaegui[1,2], Lorenzo Vallan[2], Daniel Ruiz-Molina[2], Claudio Roscini[2], Jordi Hernando[1]

[1]Departament of Chemistry, Universidad Autónoma de Barcelona, Cerdanyola del Vallès, 08193, Spain
[2]Catalan Institute of Nanoscience and Nanotechnology (ICN2) and The Barcelona Institute of Science and Technology (BIST), Cerdanyola del Vallès, 08193, Spain.

* *marc.villabona@uab.cat*

Smart windows (SWs) are among the main strategies proposed to enhance energy efficiency in buildings and lower their impact on greenhouse gas emissions.[1-3] By adapting solar radiation transmittance to weather conditions, SWs allow control of light and energy fluxes between outdoors and indoors, thus reducing the need for air conditioning and artificial lighting and increasing user's comfort. However, current SW devices suffer from severe drawbacks that hamper their broad use, such as high prices, low photostability and lack of intrinsic capacity to enable both self-regulation and user control of light transparency.[1,4-5] To overcome these limitations, herein we report a novel strategy towards SWs based on polymer films loaded with paraffin nanoparticles.[6] Proper selection of these components allows refractive index matching when the paraffin nanoparticles are in their solid state - i.e., high visible and near-infrared light transparency -, which is lost after melting, thereby resulting in pronounced light scattering - i.e., opacity. As a result, these films show ample modulation of sunlight transmittance upon thermal, photothermal and electrothermal heating (Figure 1). Several improvements result from this approach that should make our technology very appealing for the SW and other related markets (e.g., transportation windows, awnings, greenhouses): facile preparation from low-cost materials; high photostability, flexibility and scalability; fine tunability of their response; and the capacity to trigger transparency changes with user-controlled stimuli (low voltages) and relevant environmental conditions (sunlight, ambient temperatures). Actually, when tested on house models, our SW films allow high sunlight transmission in cold weather while efficiently reducing solar heat gain indoors in sunny hot days.

***Figure.** Transparent-to-opaque transitions achieved in our SW materials upon temperature variation, sunlight illumination and application of external voltages.*

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OC28

Unravelling the Excited State Deactivation Mechanisms of Indirubin and Its Role in Metabolic and Oxygen Imaging in Living Cells

Daniela Santos[1,2]*, Estefanía Delgado-Pinar[1,3], Carla Cunha[1], Nilanjon Naskar[2], Kirsten Reess[2], Adelino Galvão[4], Angelika Rueck[2], J. Sérgio Seixas de Melo[1]

[1]University of Coimbra, CQC-ISM, Department of Chemistry, P3004-535 Coimbra, Portugal
[2]University Ulm, ZBMF, Helmholtzstrasse 8/1, 89081 Ulm, Germany
[3]Molecular Science Institute, Inorganic Chemistry Department, University of Valencia, C/Catedrático, José Beltrán 2, 46980, Paterna, Valencia, Spain
[4]Centro de Química Estrutural, Instituto Superior Técnico, 1049-001, Lisboa, Portugal

daniela.santos@uni-ulm.de

Indirubin (INR), an isomer of indigo and a key component of *Danggui Longhui Wan* - a herbal mixture used in traditional Chinese medicine -, has been studied as an anti-cancer agent for the past 50 years. However, until recently, there has been a lack of understanding of its mechanisms of action, as well as its photophysical and photochemical properties [1]. Therefore, this work aims to contribute to the photochemical and photophysical characterisation of indirubin, with a focus on its remarkable photostability. Although the nature of this photostability is poorly understood, this work proposes that it is likely to be related to efficient dark processes that dominate excited state deactivation, such as the possible occurrence of excited state proton transfer, together with the potential for rotation around the central carbon-carbon bond (resulting in the formation of a *syn*-rotamer). To elucidate this behaviour, a comprehensive excited state characterisation of INR and its derivatives has been carried out. This was achieved by a combination of steady-state, fast-transient absorption, and fluorescence techniques, together with TDDFT electronic calculations [1, 2].

Using the combination of two-photon excited FLIM and PLIM techniques together with TCSPC detection, we have simultaneously measured NADH-FLIM and the INR derivatives-FLIM/PLIM inside living cells. We found that INR derivatives decrease NADH-FLIM τ_m, shifting cellular metabolism from oxidative phosphorylation to glycolysis. In addition, INR derivatives exhibit an oxygen-dependent PLIM/dFLIM signal, making them reliable oxygen sensors [3]. This research provides important insights into the stability and functional mechanisms of indirubin and demonstrates its potential role in biomedical applications such as metabolic and oxygen imaging.

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OC29

Photocatalytic Tandems Based on Polyoxothiometalates and Metallic Clusters for the Production of Dihydrogen

Maxime Lajoye, Nathalie Leclerc, Clément Falaise, Emmanuel Cadot, Mohamed Haouas

Institut Lavoisier de Versailles, CNRS, UVSQ, Université Paris-Saclay, 78035 Versailles, France

E-mail: maxime.lajoye@universite-paris-saclay.fr

The photocatalytic hydrogen evolution reaction (HER) involves cascade reactions starting with light excitation of a photosensitizer to transfer an electron to a proton reduction catalyst and ending with regeneration of the photocatalytic system through a sacrificial electron acceptor/donor agent, as illustrated in Figure. The most effective molecular photosensitisers known for homogeneous catalysis are noble metal complexes. In this study, we investigate the potential of luminescent metal clusters and thio-polyoxometalates (ThioPOMs) as Nobel metal-free photocatalytic tandem in homogeneous HER. The ThioPOMs, [1-3] which combine a lacunary polyoxometalate and the aquo cluster $[Mo_3S_4(H_2O)_9]^{4+}$, are known to be efficient catalysts for HER.[4] Our ambition is therefore to use ThioPOMs in conjunction with octahedral molybdenum clusters of the $M_6X_8L_6$ variety to act as photosensitizers [4] to replace the more expensive iridium or ruthenium-based photosensitizers. Here, we report the synthesis and multinuclear NMR characterization of ThioPOMs as well as HER photocatalytic activity in organic solutions and organic-water mixtures using different clusters as photosensitizers. The results are compared with previous work on equivalent systems [5] and discussed in terms of the hydrolytic stability effects of the clusters and ThioPOM catalysts in the media studied. Finally, the crystal structures of new CLUSPOM compounds, salts of cationic octahedral metal clusters and anionic POMs, are also obtained and can serve as models for cluster-ThioPOM catalyst tandems.

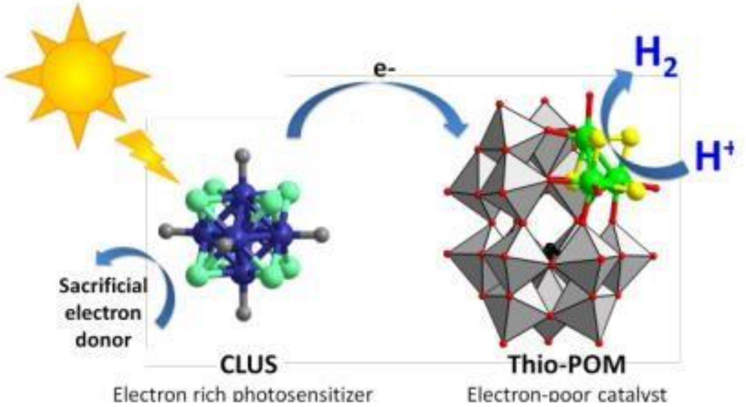

Figure: CLUSThioPOM induced electron transfer process for HER

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OC30

Shedding light on low-to-high-density fluctuations in liquid water through upconversion thermometry

Dr. Fernando E. Maturi[1]*, Ramon S. Raposo Filho[1], Prof. Carlos D. S. Brites[1], Prof. Luís D. Carlos[1]

[1]Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, Aveiro, 3810-193, Portugal

**maturi@ua.pt*

Liquid water is the primary constituent of the human body and covers the majority of Earth's surface, playing fundamental roles in various industrial and biological processes.[1] Despite its ubiquitous use as a solvent, water remains a mysterious substance with properties that deviate significantly from those of other commonly used liquids. In recent decades, researchers have discovered two distinct organizations of water molecules in the supercooled regime: a spacious low-density liquid (LDL) with a more organized tetrahedral hydrogen-bonding structure, and a tightly connected high-density liquid (HDL) with a distorted tetrahedral configuration.[2] Therefore, fluctuations between these two water motifs under ambient conditions may explain the anomalous behavior of water. In this sense, we present an experimental approach designed to investigate the Brownian velocity of upconverting nanoparticles (UCNPs) suspended in water.[3] By examining the temperature-dependent Brownian velocity, which arises from the thermal motion resulting from particle-solvent interactions, we may gain valuable insights into the temperature dependence of the hydrogen-bonding network in the vicinity of the UCNPs.

In this work, we demonstrate the feasibility of using UCNPs as nanoprobes to detect distinct water motifs that are challenging to observe in bulk water under ambient conditions. Furthermore, a crossover temperature (T_c) was identified from the bilinear trend of the temperature-dependent Brownian velocity of water-suspended UCNPs. This T_c corresponds to the transition from LDL to HDL organizations in water and is not observed when UCNPs are suspended in other solvents containing hydrogen bonds, such as ethanol and heavy water. Moreover, T_c increases as the size of the UCNPs decreases, indicating that LDL motifs exist in a distribution of sizes, making it difficult to observe the LDL-to-HDL conversion at higher temperatures. The obtained results are in good agreement with the hypothetical phase diagram depicting the singular behavior of liquid water in terms of LDL and HDL motifs at varying pressure and temperature.[4] These findings are extremely relevant because they provide experimental evidence of the existence of two organizations of water molecules under ambient conditions, suggesting that the life-supporting conditions we know may depend on two kinds of hydrogen bond organization in liquid water.

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OC31

Fluorescence Modulation by Cascade Effect in Photochromic Microcapsules

Magin Benedict Ferrer[1,2]*, Daiyu Harada[1], Colin J. Martin[1], Rémi Métivier[2], Clémence Allain[2], Keitaro Nakatani[2], Marine Louis[1], Kazuma Yasuhara[1], Tsuyoshi Kawai[1]

[1] Graduate School of Science and Technology, Nara Institute of Science and Technology, NAIST, 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan
[2] Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, 91190, Gif-sur-Yvette, France
* *magin.ferrer@ens-paris-saclay.fr*

Well-designed combinations of fluorescent and photochromic molecules can lead to fluorescent photoswitches. In order to enhance their sensitivity, our strategy is to take advantage of two phenomena: the redox-triggered cascade effect (CE) of photochromic molecules as evidenced in solution,[1] and amplified fluorescence photoswitching (AFPS), which occurs when photochromic and fluorescent molecules are at distances shorter than the Förster radius.[2] In this communication, we report on microcapsules containing fluorescent **Nile Red** and a photochromic terarylene derivative **TA0** (see Fig. 1). Some terarylene derivatives undergo a highly efficient oxidative cycloreversion of the closed form isomer (CF) *via* CE, with quantum yields above unity during the ring-opening reaction. A thorough investigation in different solvents enabled us to improve wavelength selectivity by replacing chloroform with chlorobenzene, increasing the cyclability of the fluorescent-photochromic system. Next, in order to observe both CE and AFPS, microencapsulation of **Nile Red** and **TA0** was successfully carried out. The photoswitching properties of this system will be presented together with further analysis on its kinetics.

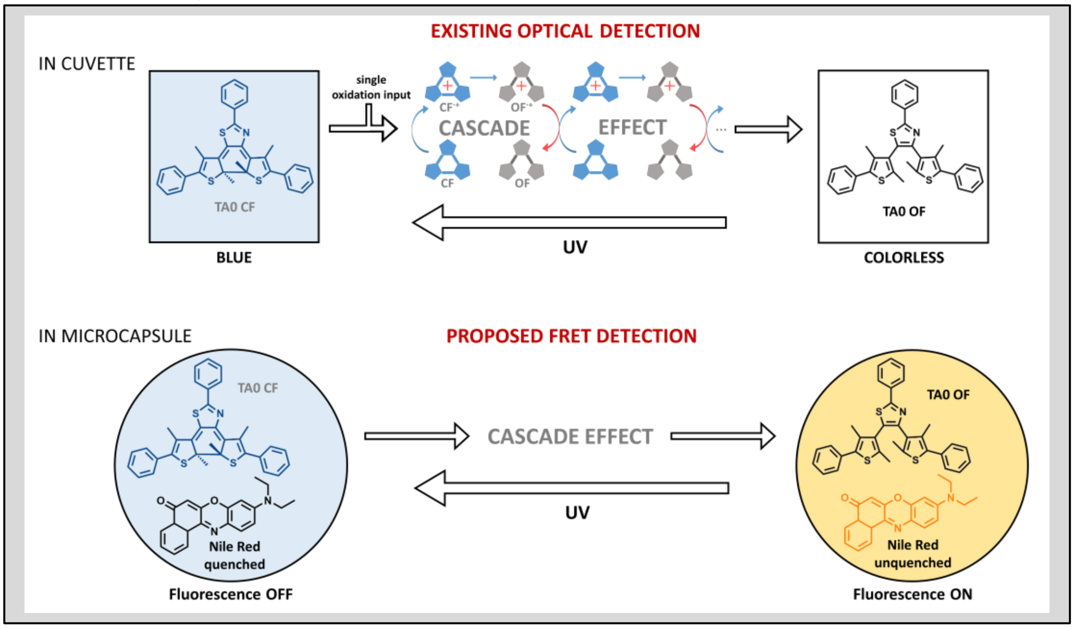

Figure 1. ***Top***: *Illustration of cascade effect system using* ***TA0*** *in bulk solution*[1]; ***Bottom***: *Illustration of the proposed cascade effect system in microcapsule with* ***TA0*** *and* ***Nile Red***.

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Poster Presentations

PP1

Chromophores-based dithienylethenes: Toward all-optical non-destructive molecular systems

Marie Barale,[1] Muriel Escadeillas,[1] Gregory Taupier,[1] Yann Molard,[1] Clément Orione,[1] Elsa Caytan,[1] Rémi Métivier[2] and Julien Boixel*[1]

[1] Université de Rennes, ISCR - UMR 6226, ScanMAT – UAR 2025, F-35000 Rennes, France.
[2] Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSMUMR 8531, 91190 Gif-sur-Yvette, France
** Julien.boixel@univ-rennes.fr*

Luminescent molecules are present in a wide variety of domains, such as biology (bio-imaging), optoelectronics (data processing, molecular storage) and electroluminescent devices that are now part of our daily lives (OLED screens). The photo-control of the luminescence property appears crucial for numerous applications, giving rise to all optical molecular systems. In the particular field of data storage and processing, the use of photoactivatable molecule is seen as a promising and sustainable solution due to miniaturization and less energy intensive. In this highly competitive field, our approach aims to the control of the luminescence by photoinduced molecular movement.

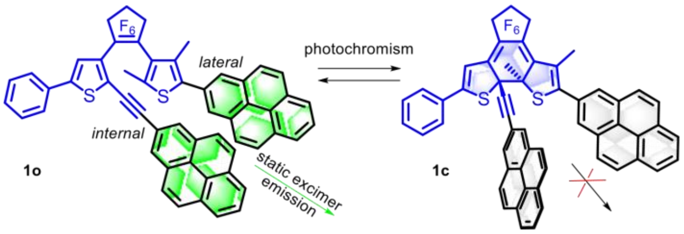

Figure. Representation of the photo-modulation of the static excimer emission.

Based on our expertise in the synthesis and study of functionalized photochromic dithienylethenes (DTE),[1] we designed new pyrene-based DTE where the two pyrenes are positioned in a face to face fashion to produce an excimeric emission upon excitation, only in the DTE's open form. The photochromic reaction of the DTE will reversibly switch the excimeric luminescence, in a chiral environment.[3] Furthermore, the all optical nondestructive readout was reached by combination of one and two photon excitation.

The design strategy and the synthetic pathways, along with the optical properties at the ground state (UV-vis) and excited state (emission) of the synthetized molecules will be presented. The results of the study of the dynamic of the system by NMR analysis and DFT calculations will be discussed.

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PP2

Photodegradation of food dyes using bio-silica supported silver nanoparticles

Andreia Costa-Tuna*, Gabriel Ribeiro, Adelino Pereira, Aklima H. Kakon, Otavio A. Chaves, José Carlos Neto-Ferreira, Carlos Serpa

[1]CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535, Coimbra, Portugal

[2]Institute of Chemistry, Department of Organic Chemistry, Federal Rural University of Rio de Janeiro, Rodovia BR-465, Km 7, 23.890-000 Seropédica, RJ, Brazil

* *andreia.dacostatuna@gmail.com*

Catalysis offers a novel approach to tackling energy and sustainability challenges. Silver nanoparticles (AgNPs) are highly active and selective nanocatalysts that require low energy consumption and have a long lifespan. For AgNPs to be effective in any application, they must maintain long-term stability. Aggregation of AgNPs can significantly reduce their effective surface area, leading to a reduction or complete loss of their catalytic properties[1]. Various stabilizing compounds are used to prevent AgNP aggregation. This project focuses on synthesizing stabilized AgNPs, initially with polyvinylpyrrolidone (PVP) and subsequently with bio-silica, which offers the additional advantage of reusability[2]. The AgNPs will be employed to photodegrade three food dyes that contribute to water pollution[3]: Amaranth, New Coccine, and Tartrazine. The silver nanoparticles were synthesized using the reduction method[4] and characterized using UV-vis spectroscopy and transmission electron microscopy (TEM). Photodegradation was induced using a Luzchem LED illuminator with a blue LED head emitting radiation at 450-460 nm. Complete photodegradation with PVP-stabilized AgNPs was achieved in 15-20 minutes using a power of 120 mW/cm^2. To compare results with the literature, the power was reduced to 16 mW/cm^2, achieving complete photodegradation in one hour—faster than other studied photodegradations using catalysts like TiO_2 nanoparticles[5]. The final step was to support AgNPs on bio-silica and study their catalytic activity to compare with the results obtained using unsupported AgNPs.

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PP3

Sulfate Radical Anion and Reactive Chlorine Species in Seawater Drug Removal

Luciana C. Schmidt*, Alberto Blazquez-Moraleja, Maria Luisa Marin, and Francisco Boscá

Instituto de Tecnología Química, Universitat Politècnica de València- Consejo Superior de Investigaciones Científicas (UPV-CSIC) Avda. de los Naranjos s/n, 46022, Valencia, Spain.
* *lcschmid@itq.upv.es*

Coastal seawater near big cities has received widespread occurrence of pharmaceuticals. Some pharmaceutical compounds are primarily resistant to photo-degradation. Among the various treatment options, advanced oxidation processes (AOPs) have been suggested as alternative treatment strategies for eliminating toxic and persistent contaminants. Moreover, sulfate radical anion ($SO_4{\bullet}^-$) based advanced oxidation has some unique features, enabling the degradation of recalcitrant compounds that are refractory to hydroxyl radical (•OH). The reactive species are produced by the activation of peroxidisulfate (PDS) or peroxymonosulfate (PMS).[1] However, most studies were performed in freshwater; in seawater, $SO_4{\bullet}^-$ and HO• are rapidly consumed by Cl^-, producing reactive chlorine species (RCS) such as chlorine atoms (Cl_2), chorine radicals (Cl•), dichlorine radical anions ($Cl_2{\bullet}^-$).[2] The generated reactive chlorine species (RCS) present different reactivity and selectivity in the degradation of contaminants.

The current study presents results from experiments designed to examine the degradation of pharmaceuticals such as diclofenac or ranitidine in the presence of $SO_4{\bullet}^-$ (Figure 1). The aims of this study were to characterize the degradation of pharmaceuticals, including a comparison of rates determined in freshwater and seawater. Care was taken in the potential toxicity of the products formed. The study found that advanced oxidation processes, particularly those based on sulfate radical anion, can effectively degrade pharmaceuticals in seawater, but the rapid consumption of reactive species by chlorine in seawater presents a challenge. These findings have significant implications for the field of environmental science and water treatment, particularly in understanding the behavior of pharmaceuticals in seawater and the potential risks associated with their degradation products.

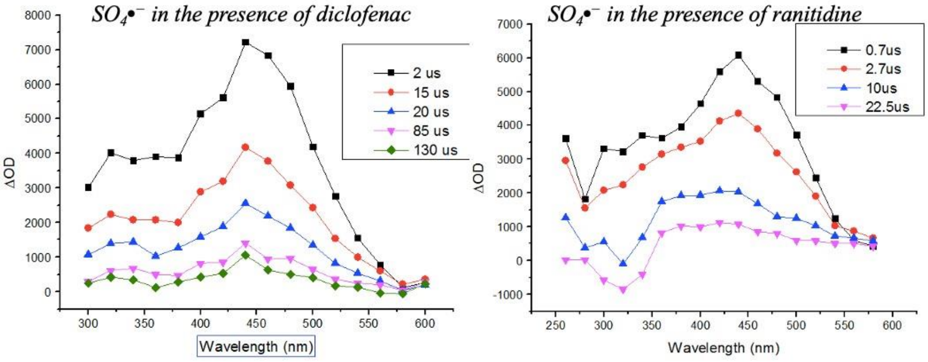

Figure 1. *Laser flash photolysis spectrum of $SO_4{\bullet}^-$ in the presence of diclofenac or ranitidine.*

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PP4

Broad-Spectrum Antimicrobial Fabrics via Photodynamic Action

Alberto Blazquez-Moraleja[1]*, M. Luisa Marin[1], Francisco Bosca[1], Inés Martínez-González[2], Pilar Moya[3], Inmaculada Andreu[4] and Marilés Bonet-Aracil[2].

[1]Instituto de Tecnología Química (Universitat Politècnica de València- Agencia Estatal Consejo Superior de Investigaciones Científicas), Spain. [2]Departamento de Ingeniería Textil y Papelera, Universitat Politècnica de València, Spain. [3]Centro Ecología Química Agrícola, Instituto Agroforestal Mediterráneo, Universitat Politècnica de València, Spain. [4]Unidad Mixta de Investigación Universitat Politècnica de València -Instituto de Investigación Sanitaria (IIS) La Fe, Hospital Universitari i Politècnic La Fe, Valencia, Spain.

* *ablamor@itq.upv.es*

Textile-derived heterogeneous photocatalysts have become key players in disinfection protocols, especially in response to increasing antibiotic resistance. Despite their growing importance, research on improving their efficacy remains scarce. To address this issue, we dyed polyamide fabrics (PAF) with various concentrations of the anionic photosensitizer Rose Bengal (RB) at 0.5%, 1%, and 3% on the weight of the fabric (o.w.f.). Among them, only fabric dyed with 1% RB showed substantial efficacy in inactivating Gram-positive bacteria under visible light, achieving a 6 $\log_{10}$ reduction in cfu/mL. Photophysical and photodynamic studies revealed that 0.5% RB-PAF showed limited bacterial inactivation due to the low concentration of RB, while 3% RB-PAF showed reduced efficacy, due to chromophore aggregation and electrostatic repulsion with the bacterial surface. To enhance microbial attraction, a cationic fixative (CF) was introduced into the 1% RB-dyed fabric. The resulting CF-RB-PAF exhibited remarkable antimicrobial efficacy against a broad range of pathogens, including Gram-positive and Gram-negative bacteria, fungi, and viruses under visible light irradiation, demonstrating its versatility and potency (Fig. 1). In addition, photodynamic studies revealed that the presence of CF increases the efficacy, improves the photostability and recyclability of RB-PAF, probably due to alterations in type I and II photooxidation mechanisms.

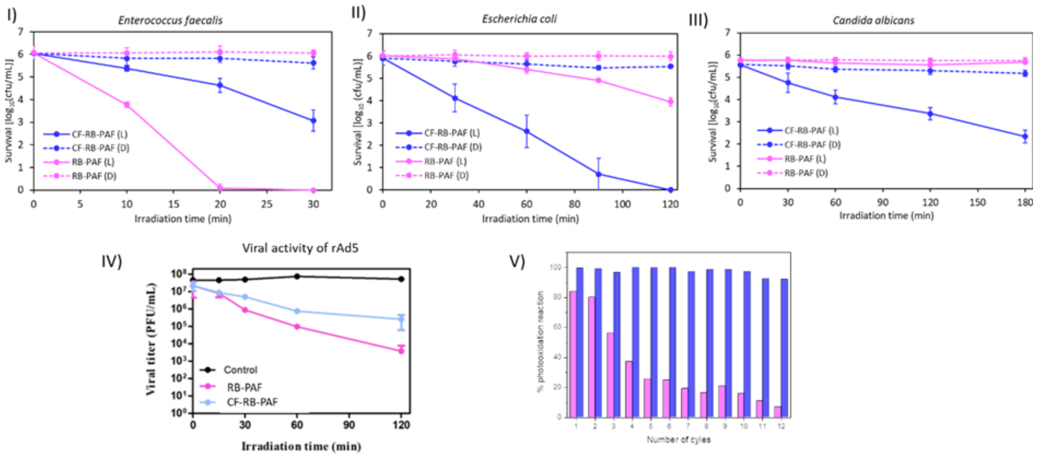

Figure 1. *Reduction of the survival of Gram-positive (I) and Gram-negative bacteria (II), fungi (III), viruses (IV), and recyclability in the photooxidation reaction of 9,10-dimethyl anthracene (V), using RB-PAF (pink) and CF-RB-PAF (blue) under dark (D) and white light irradiation (L) conditions.*

PP5

Donor-Acceptor Anthraquinone Derivatives as Versatile and Efficient Photosensitizers for Dye-Sensitized Solar Cells

Ricardo C. Pereira[1]*, Marta Pineiro[1], J. Sérgio Seixas de Melo[1]

Department of Chemistry, CQC-IMS, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

* rcpereira@uc.pt

The development of technologies and materials to harness energy from renewable sources is of great importance today. This is not only because of the challenge of combating the production of greenhouse gases resulting from the exploitation and use of fossil fuels [1], but also because of the need to reduce the emission of pollutants that threaten public health. One way of converting solar energy into electricity is to use dye-sensitised solar cells [2]. The efficiency of this conversion is largely due to the dye used in the cell. Recently, organic donor-acceptor systems have emerged as promising candidates for sensitising solar cells, as they allow efficient charge transfer without the use of rare metals [3]. The ability to incorporate different donor groups allows the absorption properties of the dye to be tailored, extending into the spectral regions where sunlight is most abundant. Anthraquinones are a family of aromatic organic compounds that can be extracted from plants and have multiple applications, including as pigments for paints and in therapeutic contexts [4]. The aim of this study was to develop new donor-acceptor systems based on 9,10-anthraquinone. To this end, donor-acceptor-π-anchor (D-A-π-A) unsymmetrically substituted anthraquinone (ATQ) derivatives functionalized with bromine (Br), diphenylamine (DPA) and indoline (Ind), BrATQBzOH, DPAATQBzOH and IndATQBzOH respectively, were synthesised and used in real DSSCs devices (Figure 1). The study included spectral characterisation in solution and on film (TiO_2), which provided cell parameters such as V_{oc}, J_{sc}, FF and PCE. The results were rationalised in terms of the influence of the donor group and the charge transfer process, supported by a TD-DFT study.

Figure 1: *Pictures of the obtained DSSC and respective anthraquinone based photosensitizers studied in this work. PCE are also given.*

Acknowledgements

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PP6

β-Amyloid autofluorescence as a tool for oligomerization studies

Jesús Seijas[1]*, Sara Illodo[1,2], Flor Rodríguez-Prieto[2], Carla Lora Parra[1], Wajih Al-Soufi[1], Mercedes Novo[1]

[1]Departamento de Química Física, Facultade de Ciencias, Campus Terra, Universidade de Santiago de Compostela 27002, Lugo, Spain.

[2]Facultade de Química, Departamento de Química Física, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

* *jesus.seijas@rai.usc.es*

Alzheimer's disease (AD) is a progressive neurodegenerative disease characterized by amyloid plaques and neurofibrillary tangles in the brain tissue resulting from protein aggregation. The detrimental consequences of amyloid aggregation within the human body are believed to instigate a cascade of events leading to neurotoxicity, synaptic dysfunction, and ultimately, cognitive decline.[1,2] Understanding the underlying mechanisms of amyloid (Aβ) aggregation, especially at the early stages, is vital for the development of effective therapeutic strategies aimed at preventing or halting the progression of AD. Our group has studied this early aggregation using Fluorescence Correlation Spectroscopy (FCS), which allows the determination of the fraction of aggregated amyloid of the sample and the true total amyloid concentration and the characterization of the aggregates formed.[3-5] However, there is a need for detection and quantification methods of the amyloid aggregation degree based on conventional fluorescence techniques, which could be used in standard laboratories. Therefore, the aim of this work is to design a strategy to detect and characterize Aβ oligomers based on the autofluorescence of amyloids. We present preliminary results of the variation of Aβ fluorescence spectra with oligomerization and compare them with those obtained by (FCS).[5]

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PP7

Synthesis of indolizine-based hemicyanine fluorophores with bulky counter-anion for two-photon near-infrared imaging

Marie Lucas[1]*, Yann Bretonnière[1]

[1]Functional materials and photonics axis, Laboratoire de Chimie, ENS Lyon, Lyon, France
* *marie.lucas1@ens-lyon.fr*

Biological materials exhibit transparency in several near-infrared (NIR) therapeutic windows called NIR-1 (700-900nm), NIR-2 (1000-1500 nm) and NIR-3 (approximately 1700nm). Fluorophores with absorption and emission wavelengths in these windows allow for deeper and clearer imaging than visible light fluorophores.[1,2,3] Over the years, our lab has developed D-π-A dipolar fluorophores for two-photon excitation microscopy, a deeper and less damaging imaging technique that shifts the absorption into the NIR.[4,5,6] In this context, we have recently focused on electron-rich nitrogen heterobicycles with a bridgehead nitrogen, such as indolizine (pyrrolo[1,2-a]pyridine), as strong donor group (D) and have obtained far-red emitters.[7,8]

In the work presented here, we have sought to increase the Stokes shift of indolizine-based fluorophores in order to reach the NIR. We elongated the π-bridge and focused on strong cationic N-heterocyclic acceptors (A) to red-shift the optical properties of the fluorophores, thus obtaining hemicyanines with tunable solubility properties depending on the counter anion.

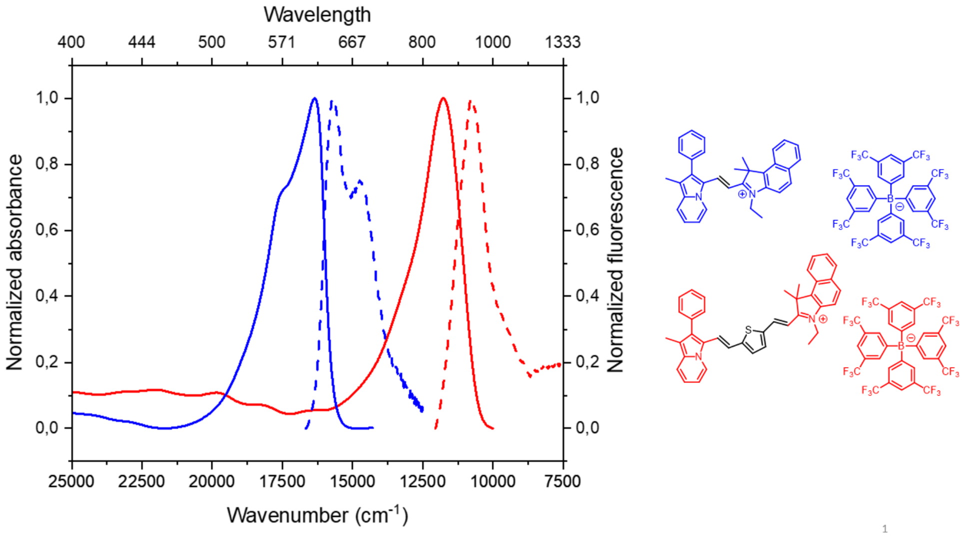

Figure. *Example of red-shifting with an elongated π-bridge.*

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PP8

Thiazole Orange and Proflavine as Fluorescent Probes for dsDNA Detection

Stella Hernández[1]*, Sofía Castro[1], Lucas Piñeiro[1], Mercedes Novo[1], Wajih Al-Soufi[1] 1

Departamento de Química Física, Facultade de Ciencias, Campus Terra, Universidade de Santiago de Compostela, E-27002 Lugo, Spain

* *stella.hernandez@rai.usc.es*

Thiazole Orange (TO) and Proflavine (PR) are DNA intercalating dyes potentially useful for the detection and quantification of double-stranded DNA (dsDNA). TO is almost non-fluorescent in an aqueous solution but exhibits significant fluorescence upon binding to dsDNA. Conversely, PR's fluorescence intensity decreases when it binds to dsDNA.

High affinity constants have been documented for the complexation between TO and PR with dsDNA[1] and the sequence selectivity of TO has been examined to assess its potential application in fluorescent intercalator displacement assays.[2,3] Additionally, the interaction of TO with other DNA conformations has been reported.[4]

In this study, we use steady-state fluorescence to examine the supramolecular association between these two intercalators and dsDNA. The affinity of these intercalating agents for dsDNA varies depending on experimental conditions, particularly the charge and concentration of the ions in the solution.[5, 6] These effects on the binding equilibrium constant were systematically investigated using NaCl and MgCl$_2$ and explained based on salt activity and cation charge. The consequences of these salt effects on dsDNA quantification are discussed.

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PP9

Effects of π-extension with aldehydes, imines and carboxylic acids on HTI photoswitches

Matías I. Quindt[1]*, Stefano Crespi[1]

[1]Department of Chemistry - Ångström Laboratory, Uppsala University, Sweden.
*_matias.quindt@kemi.uu.se_

Hemithioindigo (HTI) chromophores belong to the emerging class of indigoid photoswitches and have garnered significant attention for their versatility as photoswitch molecules. They exhibit responsiveness to visible light, distinct absorption variances between their photoisomers, high thermal stability of metastable states, and facile synthetic accesibility.[1]

This study explores novel HTI derivatives created by introducing formyl and carboxy groups at the *para* position of the stilbene fragment (**1-2** see on Figure). This modification aims to broaden the chemical diversity and potential applications of HTI-based photoswitches, enabling tailored properties and functionalities in light-responsive materials. Additionally, to enhance the acceptor strength of the thioindigo fragment, we decide to explore different levels of *S*-oxidation, resulting in sulfoxide derivatives (**3-4**), and the sulfone derivative **5**. Taking advantage of the reactivity of the incorporated aldehyde group, an aromatic imine **6** was synthesized to mimic a reaction scenario that could occur within biological systems, such as forming a Schiff base upon reacting with a nitrogenous residue. The goal of obtaining this imine was to provide two photoswitchable groups for potential applications. These derivatives were studied for their photoresponsive behavior to visible light under various irradiation wavelengths and solvent conditions, as well as their thermal back-isomerization. The UV/Vis spectra exhibited a hypsochromic shift post-sulfur oxidation. Kinetic parameters of thermal decay for *E*-isomers were determined, indicating that sulfur oxidation had minimal impact on thermal back-isomerization, thereby maintaining a high barrier for bistable photoswitching across diverse applications.

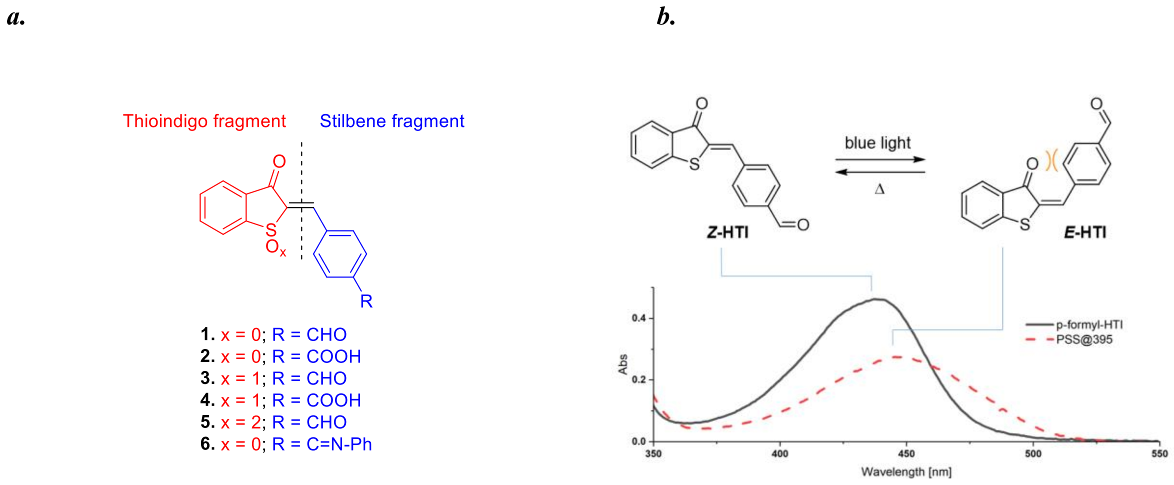

Figure.a. HTI's photoswitches synthesized. ***b.*** UV/Vis spectra of *Z*-HTI-**1** (solid line) and *E*-HTI-**1** (dashed lines).

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PP10

Photophysical and spectroscopic characterization of methyl-substituted ladder-type(*meta*-phenylene) compounds

Paulo D. Nunes Barradas*, Hauke J. Jötten[2], Ullrich Scherf[2], J. Sérgio Seixas de Melo[1]

[1]University of Coimbra, CQC-ISM, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal
[2]Bergische Universität Wuppertal, Macromolecular Chemistry Group (buwmakro) and Wuppertal Center for Smart Materials and Systems (cm@s), Gauss-str. 20, D-42119, Wuppertal, Germany

* *paulond2612@gmail.com*

Conjugated ladder structures are recognized as a distinct class of materials with remarkable properties such as stiffness, enhanced thermal stability, and extended π-conjugation, leading to unconventional optoelectronic properties.[1] In this work, the photophysical and spectroscopic characterization of an octameric methyl-substituted ladder-type macro(meta-phenylene) (MeLMMP) and its analog, the ladder-type poly(meta-phenylene) polymer, (MeLPMP)[2], has been carried out in both solution and solid states; see structures in Fig.1. In solution, both the octameric and polymeric samples exhibited very similar optical spectral profiles with relatively small Stokes shifts. Time-resolved measurements in solution showed these to be fitted to bi- and tri-exponential fits depending on the compound (MeLMMP or MeLPMP) and emission wavelength. The absorption and emission spectra of MeLMMP showed inhomogeneous broadening due to potentially different isomers resulting from the ring closure of the macrocycle during synthesis (Fig. 1). The number and most probable structures of these are discussed. The energies of the singlet and triplet excited states were also obtained at 77 K for both compounds, MeLMMP and MeLPMP. The solid-state MeLMMP exhibited a spectral profile similar to that observed in solution, with fluorescence lifetime experiments revealing a bi-exponential decay fit, in contrast to the behavior observed in solution.

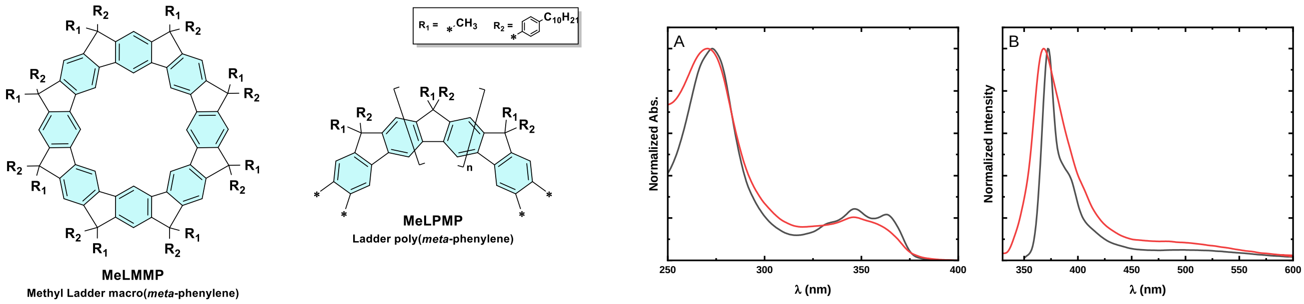

Figure 1. *(left) Chemical structures of ladder-type macro(meta-phenylene) (MeLMMP) and ladder-type poly(meta-phenylene) (MeLPMP). (right) Normalized (a) absorption and (b) emission spectra of (red) MeLMMP and (black) MeLPMP in MCH at 298 K*

Acknowledgements
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PP11

Micropatterning and Photosculpting of Silver Nanoparticles for Enhanced Luminescence

M. Carmen Gonzalez-Garcia[1]; Emilio Garcia-Fernandez[1]*; Jose L. Hueso[2]; Pedro M. R. Paulo[3]; Angel Orte[1]

[1] Department of Physical Chemistry, University of Granada, Calle del Profesor Clavera s/n, 18012 – Granada, Spain.
[2] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Campus Rio Ebro, 50018 – Zaragoza, Spain.
[3] Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal.

Abstract

Controlling the nano- and micropatterning of metal structures is essential for various technological applications in photonics and biosensing. This study presents a novel method for creating silver micropatterns through laser-induced photosculpting [1].

The process is driven by plasmonic interactions between pulsed laser radiation and silver nanorods (AgNRs) in aqueous suspension. These interactions result in optical binding forces [2-5] that transport the AgNRs, while electronic thermalization causes photooxidation, melting, and ripening of the AgNRs into well-defined 3D-structures, termed "*Airy castles*" due to their resemblance to diffraction-limited Airy disks. These structures contain emissive silver nanoclusters, allowing for the visualization of the aggregation process using luminescence microscopy. The study examines key factors influencing the photosculpting process, including the concentration and shape of AgNRs, as well as the laser's energy, power, and repetition rate. Additionally, the potential applications of these Airy castles are explored by measuring the metal-enhanced luminescence [6] of a europium-based luminophore.

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PP12

Photophysical Properties of Triazacyclononane Complexes with Thioanisolyl-Picolinate Chromophores as a Function of the Lanthanide Ion

Salauat R. Kiraev[1]*, Dina Akl,[1] Lucile Bridou,[1] Maher Hojorat,[1] Guillaume Micouin,[1]

François Riobé,[2] Sandrine Denis-Quanquin,[1] Akos Banyasz,[1] Olivier Maury[1]

[1]Univ. Lyon, ENS de Lyon, CNRS, Laboratoire de Chimie UMR 5182, F-69342 Lyon, France
[2]Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France
* *salauat.kiraev@ens-lyon.fr*

The molecular complexes of lanthanide(III) ions (Ln(III)) receive increased attention due to unique 4f-4f emission properties. The Ln(III) luminescence consists of line-like transitions emitting in the visible and near-infrared (NIR) electromagnetic spectral regions with up to ms lifetimes. Such features offer detection in a time-resolved mode and an augmented signal-to-noise ratio useful for bioimaging applications. Ln(III) have similar coordination chemistry, allowing chelation with identical macrocyclic ligands, combined with the organic chromophores, or antennae, that strongly absorb light and overcome the low Ln(III) extinction coefficient.[1]
One of the most ubiquitous chromophores for sensitising Ln(III) emission via one (1P) or two-photon (2P) absorption is the picolinate charge-transfer (CT) antenna with an electron donor on the *p*-position. The *p*-alkoxyphenyl derivatives efficiently transfer energy to the Eu(III) ions with emission quantum yields up to 48%, staining cells with optimal brightness.[2] However, the ethynyl-containing donor groups were shown to be unstable in the presence of trifluoroacetic acid[3] or undergoing a thiol-yne reaction during the peptide coupling.[4]
Thus, our objective was to prepare triple-bond deprived CT antennae by functionalising picolinates with thioanisolyl donors in a series of Ln(III) compounds with triazacyclononane (tacn, Figure 1) macrocycles. Tacn was alkylated with three thioanisolyl-picolinates, affording a new nonadentate ligand, which formed complexes with visible and NIR emitting Ln(III). The Eu(III) species had 44% quantum yield, while Tb(III) emission was quenched by oxygen due to thermal back energy transfer to the antenna triplet excited state.[5]

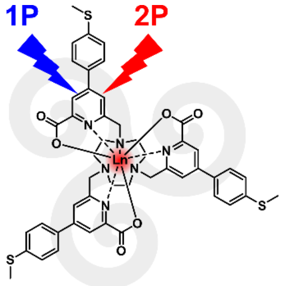

Figure 3. *The structure of target Ln(III) complexes of a new tacn-based ligand with thioanisolyl-picolinate antennae.*

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PP13

Hybrid Photoredox Catalysts for Selective Radical Chemistry

Akshay Silswal[1]*, Irina Shepeleva[1], Gediminas Jonusauskas[1], Malik Sebbat[2], Christelle Despas[4], Neus Vilà[4], Alain Walcarius[4], Bénédicte Lebeau[3], Morgan Cormier[2], Jean-Philippe Goddard[2] and Nathan McClenaghan[1]

[1]Université de Bordeaux, CNRS, France
[2]Université de Haute-Alsace (UHA), Université de Strasbourg, CNRS, France
[3]Université de Strasbourg, Strasbourg, France
[4]Université de Lorraine, CNRS, France

akshay.silswal@u-bordeaux.fr

A key aspect of enhancing the sustainability of photochemical processes, especially for large-scale reactions, is the development of recyclable catalysts to reduce waste and costs. One approach to achieve this is transitioning from homogeneous to heterogeneous catalysis by immobilizing well-defined photocatalysts onto insoluble solid-state materials. Since most organic molecules do not absorb light beyond 400 nm, visible light catalysis has emerged as a viable method for promoting chemical transformations, successfully demonstrated through photoredox catalysis.[1] Herein, we have developed heterogeneous photoredox catalysts by combining porous material with a well-defined photoredox catalyst moiety. The mesoporous silica-based [Ru]-containing and 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) containing heterogeneous photocatalysts has been achieved using a covalent grafting route. The two components are linked, with the support material acting as a redox partner in a confined environment. Lifetime of transient radical intermediates as well as photocatalyst excited states are governed by confined environment.[2] We explored the impact on excited states of photocatalyst in the confined environment. These studies provide fruitful insights on the performance and catalytic efficiency of the heterogeneous catalyst.

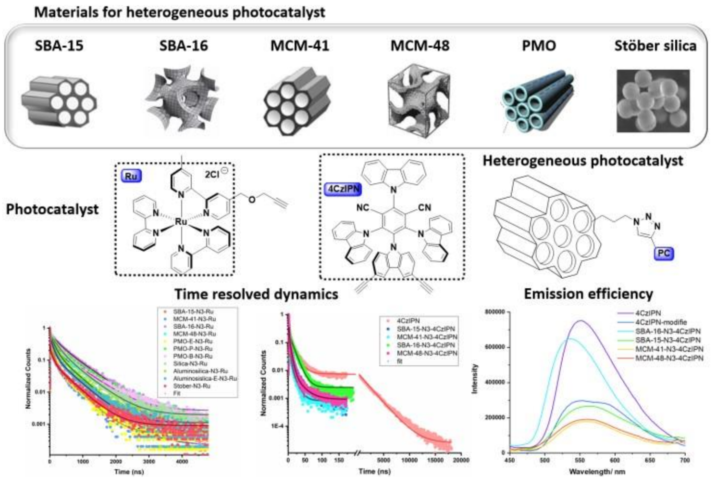

Figure. *Schematic representation of heterogeneous photocatylst and their emission dynamics* We thank the Agence Nationale de la Recherche, France (project « Photomaton-2 ») for funding.

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PP14

Ultrafast Spectroscopic Investigation on the Effect of Electron-donating Substituent Group on Excited-state Dynamics of Oxindole Photo-switches

Xingjie Fu[1]*, Matthew Mgbukwu[1], Daniel Doellerer[2], Stefano Crespi[3], Ben L. Feringa[2], Jérémie Léonard[1], Stefan Haacke[1]

[1]Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS UMR 7504, Strasbourg, France

[2]Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[3]Department of Chemistry, Ångström Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden

* *xingjie.fu@ipcms.unistra.fr*

The E-Z photo-isomerization of a C=C double-bond is the central mechanism present in a variety of synthetic photo-switches and photo-motors currently under development[1]. One crucial milestone of such development lies in the establishment of a solid link between the chemical modifications and the photo-physical properties, in particular the photo-isomerization quantum yield (Φ_{ISO}). Within this context, some of us have recently demonstrated, with the example of oxindole photo-switches (Fig. 1a), the strong correlation between the electron-donating strength of substituent groups and the Φ_{ISO}[2]. Next, to further uncover the causality behind the observed correlation, we propose the investigation via ultra-fast spectroscopy, i.e., transient absorption (TAS) and fluorescence up-conversion (FLUPS) to reveal the reaction pathways on femto- and pico-second time scales where the isomerization takes place. Here, we present the TAS and FLUPS investigation of the protonated oxindole (OxI-OH) and the deprotonated oxindole (OxI-O^-). The two protonation states represent two substituent groups, -OH and -O^-, with the electron-donating strength of -O^- twice as large as that of -OH in terms of Hammet's substituent constant[3]. Upon UV excitation, both OxI-OH and OxI-O^- manifested a sub-picosecond lifetime (~0.2 ps) and a picosecond lifetime (> 1 ps) of excited-state absorption (ESA) in TAS, as well as of the up-converted fluorescence emission in FLUPS (Fig. 1b&c). Such multiple lifetimes have previously been attributed to the population of an intermediate state, i.e., the weakly emissive so-called 'phantom state', along the reaction coordinate corresponding to the pyramidalization of the C=C double-bond[4]. The characterization of the 'phantom state' is central to our ongoing investigation on a larger set of oxindole derivatives[2], as the branching efficiency from it towards E or Z configuration is one of the fundamental roots of the Φ_{ISO}.

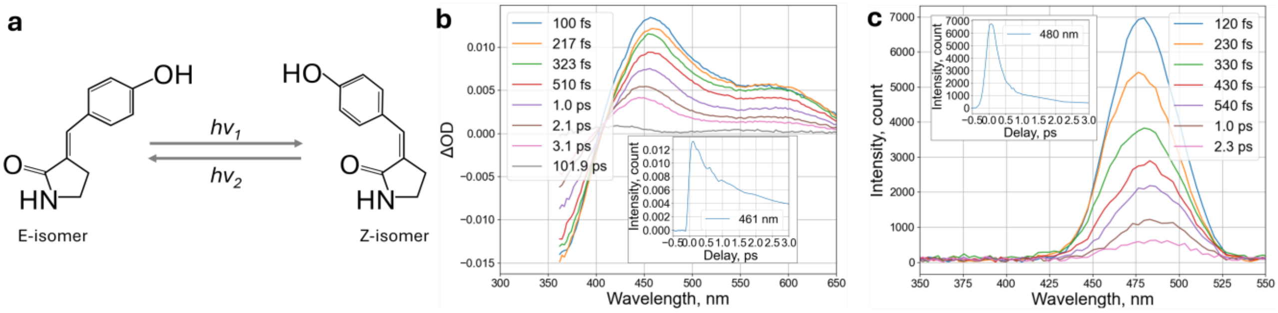

***Fig. 1. a**. E-Z photo-isomerization of OxI-OH; **b**. transient absorption spectra and **c**. upconverted emission spectra of OxI-OH. Insets in **b**. and **c**. are time traces at single wavelengths.*

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[4]

PP15

Photoinduced Processes In Octahedral Tungsten Halide Cluster And Polyoxometalates Photocatalytic Systems

Thi Huyen My Dang,[a] Clément Falaise,[b] Stéphane Cordier,[c] Mohamed Haouas,[b] Emmanuel Cadot,[b] Adèle Renaud,[c] Rachel Meallet,[a] Karine Steenkeste,[a] Thomas Pino,*[a] Minh-Huong Ha-Thi*[a]

[a] Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d’Orsay (ISMO), 91405 Orsay, France.

[b] Univ. de Versailles Saint-Quentin-en-Yvelines, CNRS Institut Lavoisier de Versailles, 78035, Versailles Cedex, France.

[c] Univ Rennes, CNRS, ISCR – UMR 6226, ScanMAT – UAR 2025, F-35000 Rennes, France.

E-mail: my.dang@universite-paris-saclay.fr; minh-huong.ha-thi@universite-paris-saclay.fr

One promising solution to the energy crisis is artificial photosynthesis (AP),[1] which mimics natural photosynthesis to convert solar energy into chemical energy carriers. However, a significant challenge in this field is the design of catalysts that are efficient, selective, recyclable, and free of noble metals. Octahedral transition-metal halide clusters made from earth-abundant elements are promising photosensitizers for their strong luminescence and long-lived triplet state.[2,3] On the other hand, polyoxometalates (POMs) are water-soluble metal-oxide discrete polyanions known for their ability to reversibly exchange many electrons (electrons reservoir)[3] making them attractive candidates for catalysis. In this study, we propose the photophysical investigation of novel systems for the production of hydrogen (HER) designed to function in water, involving the utilization of the octahedral tungsten halide cluster $[W_6I_8Cl_6]^{2-}$ as photosensitizer in conjunction with POMs such as $[PW_{12}O_{40}]^{3-}$, $[P_2W_{18}O_{62}]^{6-}$, $[BW_{12}O_{40}]^{5-}$ as catalysts (Figure 1). A complete photophysical study was conducted on $[W_6I_8Cl_6]^{2-}$ cluster and POMs tandems using steady-state absorption and emission, time-resolved emission and nanosecond transient absorption spectroscopy. The spectroscopic characteristics of the charge-separated state obtained by transient absorption spectroscopy, complemented by spectro-electrochemical experiments demonstrate the photoinduced electron transfer from the excited cluster to POMs.

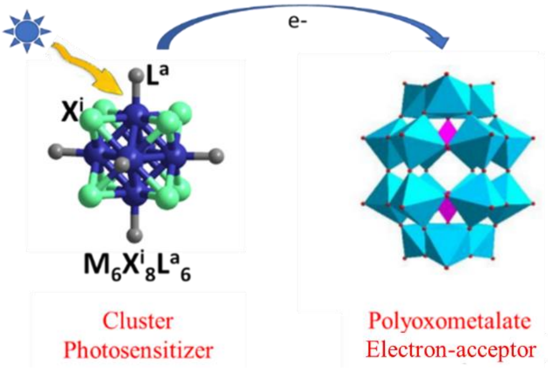

Figure 1. Photo-induced electron transfer from $[W_6I_8Cl_6]^{2-}$ to polyoxometalate

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PP16

Multi-stimuli-induced modulation of fluorescence and colour with spirocyclic Meisenheimer complexes

Anna Pozzobon[1]*, Laura Parejo[1], Marc Villabona[1], Gonzalo Guirado[1], Rosa Mª Sebastián[1], Jordi Hernando[1]

[1]Departament de Química, Universitat Autònoma de Barcelona, Carrer dels til·lers s/n, Cerdanyola del Vallès (Barcelona), 08193, Spain.

* *anna.pozzobon@uab.cat*

Spirocyclic Meisenheimer complexes (SMCs) are a new class of multi-state and multi-stimulus fluorochromic molecular switches developed in our group[1–3]. Their structures are composed of (a) a cyclohexadienyl anion bearing electron-withdrawing groups (EWGs) that confers colour and fluorescence to the system, and (b) a triazene ring capable of modulating these optical properties via acid-base or electrochemically-induced protonation and deprotonation processes as well as through temperature- or solvent-promoted ring-opening (Figure 1). This behaviour, in combination with their one-step synthesis from commercially-available phenols and carbodiimides, make SMCs very promising for the preparation of stimuli-responsive functional materials. In this work we report new advances on the development of SMC switches, which cover the following areas: (a) the optimization of their synthesis to grant access to a larger library of compounds; (b) the preparation of new SMC switches with tuneable optical properties by varying the nature of their EWGs; and (c) the introduction of reactive groups in their structure for covalent attachment to solid supports.

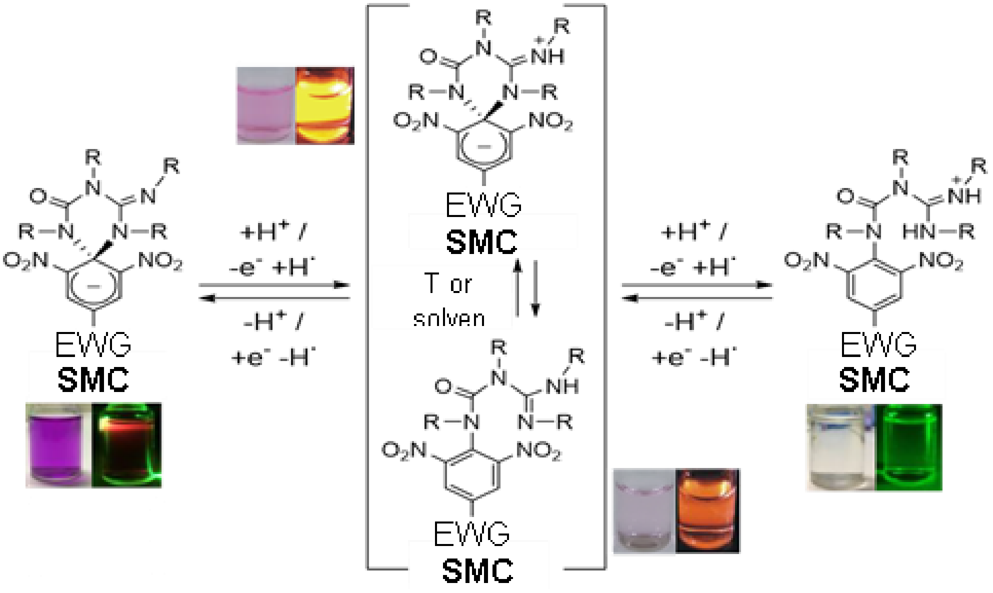

Figure 1. *Switchable behaviour of SMCs upon application of different external stimuli.*

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PP17

Fading away…or not? The photostability of ancient organic reds

Márcia Vieira[1]*, Artur Neves[1,2], Artur J. Moro[3], Vanessa Otero[1,4], Maria João Melo[1]

[1]LAQV-Requimte Research Unit, Department of Conservation and Restoration, NOVA School of Sciences and Technology, Caparica, 2829-516 Caparica, Portugal

[2]CIUCHT Research Unit, NOVA School of Sciences and Technology, Caparica, 2829-516 Caparica, Portugal

[3]LAQV-Requimte Research Unit, Department of Chemistry, NOVA School of Sciences and Technology, Caparica, 2829-516 Caparica, Portugal

[4]VICARTE Research Unit, Department of Conservation and Restoration, NOVA School of Sciences and Technology, Caparica, 2829-516 Caparica, Portugal

* *mc.vieira@campus.fct.unl.pt*

Red dyes have been a fundamental part of the color palette for millennia and give important information on the history and conservation state of historical objects[1]. In the past, the major sources were madder, cochineal, lac dye, kermes, and brazilwood, generally used in paintings as lake pigments, i.e., the chromophore is complexed with a metallic ion, usually Al^{3+}[2]. In the 19th century, even after the introduction of synthetic organic pigments, these natural colors continued to be used by renowned artists such as Vincent Van Gogh (1853-1890). Brazilwood and madder have been found in his paintings, either pure or mixed with each other [3]. At that time, it was already known that these dyes were prone to fading[1,] and interestingly, this instability was a concern for the artist[3].

When studying historical artists' materials, it is crucial to understand their original production methods, as modern materials do not accurately represent past formulations. Over the last decade, we have systematically studied the Winsor & Newton 19th Century Archive Database, demonstrating its exceptional value as a primary source of information on the practices of one of the leading paint manufacturers of the 19th century. We have investigated their manufacture for both brazilwood and madder lake pigments[4,5].

Based on the previous research, this work reproduced a set of historical recipes for brazilwood and madder lake pigments. We also prepared formulations that included their mixtures and the addition of common additives used at the time to reduce the cost of these colors. All reconstructions were characterized by colorimetry, reflectance spectroscopy, high-performance liquid chromatography with diode array detector, microspectrofluorimetry, and infrared spectroscopy (microFTIR). We explored the relation between the stability of the chromophores, their complexes and the historical formulations through the calculation of the photodegradation quantum yields ($□_R$). The knowledge obtained will be fundamental to assessing these formulations' conservation state and original colours in artworks. Furthermore, it may contribute to creating sustainable retro-engineered materials for modern applications.

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PP18

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

Saül Garcia-Orrit,[a*] Víctor Vega-Mayoral,[a] Qiang Chen,[b] Gianluca Serra,[c] Michele Guizzardi [d], Valentino Romano [d], Stefano Dal Conte [d], Giulio Cerullo [d], Lorenzo Di Mario [e], Moredechai Kot [e], Maria Antonietta Loi [e], Akimitsu Narita,[b,f] Klaus Müllen,[b,g] Matteo Tommasini,[c] Juan Cabanillas-González,[a]

[a] Madrid Institute for Advanced Studies, IMDEA Nanociencia, c/Faraday 9, Campus de Cantoblanco, Madrid 28049, Spain.
[b] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[c] Dipartimento di Chimica, Materiali ed Ingegneria Chimica "G.Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)
[d] Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo Da Vinci, 32, 20133 Milano, Italy
[e] Photophysics and OptoElectronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands
[f] Organic and Carbon Nanomaterials Unit, Okinawa Institute of Science and Technology Graduate University, Okinawa 904-0495, Japan
[g] Institute for Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

* *saul.garcia@imdea.org*

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)→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.

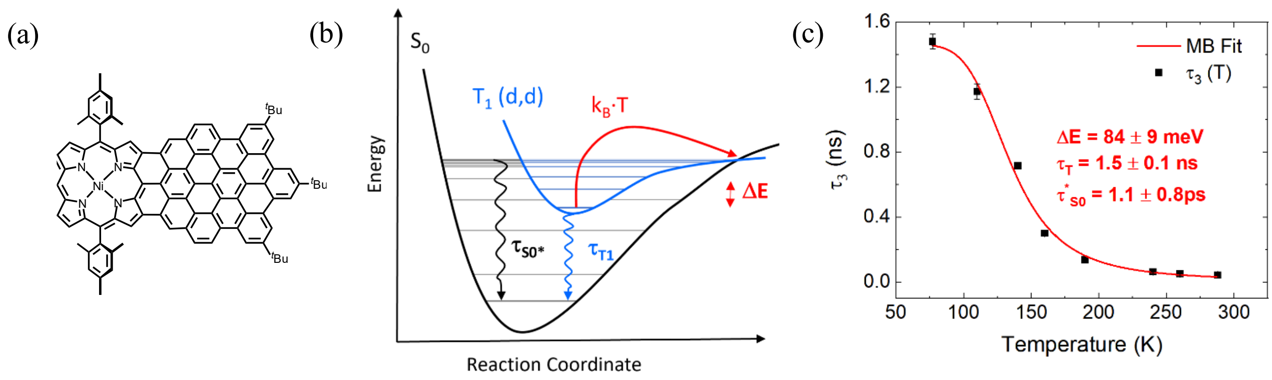

Figure. (a) Chemical structure of NP molecule. (b) Scheme of the potential energy surfaces involved in the deexcitation process on NP. (c) Value of the final relaxation lifetime as a function of temperature obtained by global fit analysis.

PP19

Optical and structural characterization of core-shell nanomaterials (SiO_2@TiO_2@AuNPs and SiO_2@AuNPs@TiO_2) for H_2 production

Zohreh Moghaddasi[1]*, Jennifer Dewalque [2], Gilles Spronck [2], Grégory Barbillon[3,4], Françoise Pillier[3], Vien-Duong Quach[1], Alireza Ranjbari[1], Mohamed Nawfal Ghazzal[1]*, Christophe Humbert[1]*

[1] Institut de Chimie Physique, Université Paris-Saclay, CNRS, UMR 8000, 91405 Orsay, France
[2] GREENMAT, CESAM Research Unit, Department of Chemistry, University of Liège, 4000 Liège, Belgium
[3] Laboratoire Interfaces et Systèmes Electrochimiques, Sorbonne Université, CNRS, UMR 8235, LISE, 4 Place Jussieu, 75005 Paris, France
[4] EPF-Engineering School, 55 Avenue du Président Wilson, 94230 Cachan, France

Hydrogen is one of the potential clean energy sources that could address two major worldwide concerns: energy crises and environmental difficulties. Hydrogen production often involves the use of fossil-based technologies, which emit a significant amount of greenhouse gases in the process. As a result, one of the primary objectives of the last several decades has been to decarbonize the industry. Finding affordable, environmentally friendly, and dependable hydrogen generation systems with minimal emissions is essential for achieving this goal [1]. Researchers studying energy production have developed a strong interest in the use of photocatalysis materials such as TiO_2 as a reliable alternative way for H_2 production. At the Institut de Chimie Physique d'Orsay (ICP), we found a promising way to increase the yield of H_2 production taking profit of a coreshell structure with two different configurations (SiO_2@TiO_2@AuNPs and SiO_2@AuNPs@TiO_2) [2]. However, the difference in H_2 yield between these two structures remains unknown and requires in-depth investigation. Using optical techniques such as surface sensitivity SFG spectroscopy can help track and monitor the steps involved in H_2 production at the surfaces of these structures. SFG spectroscopy is an *in-situ* optical probe that has succeeded in monitoring *in-situ* interfaces [3-4]. Therefore, we use the same approach on these core-shell nanomaterials to provide an exact pathway to the chemical reactions that occur during H_2 production. The core-shell nanomaterials have been synthesized and studied, and the coating optimized for SFG spectroscopy. We have used different deposition techniques (USP coating and spin coating) and substrates. Additionally, we have characterized the samples using spectroscopy techniques and SEM imaging to better understand the chemical and structural properties of these materials. At the end, our findings could potentially pave the way to have a coupled fundamental view of *in-situ* surface chemistry and could impact the field of green energy production.

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PP20

Synthesis and photophysical studies of Au(I) and Pt(II) cyano complexes

Mar García Del Amo[1]*, Guillermo Romo Islas[1,2], Laura Rodríguez Raurell[1,2]

[1]Departament de Química Inorgànica i Orgànica, Universitat de Barcelona
[2]Institut de Nanociència i Nanotecnologia (IN 2UB), Universitat de Barcelona
*mar12gda@gmail.com

Luminescence is a process that can be affected by a wide range of factors such as the concentration, the temperature, the presence of heavy atoms and metal···metal interactions, among others[1]. Heteroatoms, such as halogens, can be one of the class of heavy atoms that are observed to favor intersystem crossing, enhancing phosphorescence to the detriment of fluorescence.[2]

In this work, we have designed and synthesized several coordination chemistry compounds that contain two types of heavy atoms: halogens and heavy metals (gold and platinum). The effect of the concentration on the resulting luminescence has been also analysed, since the compounds can form supramolecular assemblies at high concentrations due to the presence of possible metal···metal and metal···ligand interactions and/or other type of weak contacts that can play a key role on their resulting photophysical properties.[3-5] Six different Au(I) and Pt(II) compounds are here present. The compounds present an angular structure and contain different substituents in the X position.

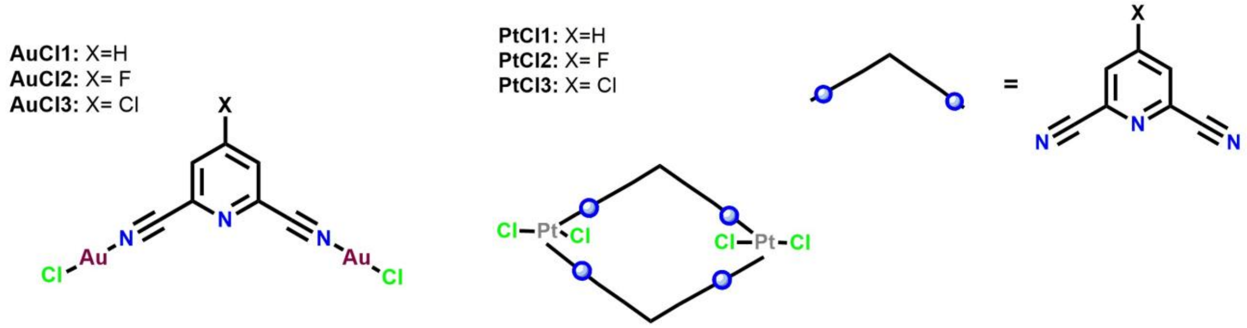

Figure. *Structres of the Au(I) and Pt(II) cyano compounds synthetized..*

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PP21

Self-assembled tetrahedral $[\mathrm{Cr^{III}}_4\mathrm{L}_6]^{12+}$ cage displaying NIR spin-flip photoluminescence

Yating Ye,[a] Iñigo J. Vitorica-Yrezabal,*[a] Carlos M. Cruz,[b] Benjamin Doistau,[c] Enrique Colacio,[a] Claude Piguet,[d] Juan Manuel Herrera,[a] Juan-Ramón Jiménez*[a]

aDepartment of Inorganic Chemistry. University of Granada and “Unidad de Excelencia en Química (UEQ)”, Avda. Fuente Nueva s/n, 18071, Granada, Spain.
bDepartment of Organic Chemistry. University of Granada and “Unidad de Excelencia en Química (UEQ)”, Avda. Fuente Nueva s/n, 18071, Granada, Spain.
cLaboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques (UMR 8601), Université Paris Cité, CNRS, 45 rue des Saint-Pères F-75006 Paris, France.
dDepartment of Inorganic and Analytical Chemistry, University of Geneva, 30 quaiE. Anserment, CH-1211 Geneva 4, Switzerland.

*yatingwsy@ugr.es

The thermodynamically controlled self-assembly of bis-bidentate quaterpyridine ligand, L = 2,2’:5’,5’’:2’’,2’’’-Quaterpyridine, with Cr(II) and subsequent oxidation to Cr(III) yields the first photoluminiscent tetrahedral $[\mathrm{Cr^{III}}_4\mathrm{L}_6]^{12+}$ molecular cage. Single crystal X-ray diffraction reveals the presence of a PF6 anion inside the cavity. Each corner of the polyhedron is occupied by weakly antiferromagnetically coupled $\{\mathrm{Cr(bipy)_3}\}^{3+}$ (bipy = 2,2′-bipyridine) patterns as reveals by magnetometry. Upon light excitation in the UV-Vis region, spin-flip luminescence from the $^2\mathrm{E}/^2\mathrm{T}_1$ excited states with maximum at 727 nm was detected at room temperature. The excited state lifetime of 183 μs is longer than 102 μs recorded for the mononuclear $[\mathrm{Cr(bipy)_3}]^{3+}$. The luminescence quantum yields are in the same order of magnitude and amount to 10^{-2} %. The photoluminescence brighness, B, goes from 14 $\mathrm{M^{-1}\cdot cm^{-1}}$ to 90 $\mathrm{M^{-1}\cdot cm^{-1}}$. This nine-fold improvement is observed across the entire excitation wavelength range and it is due to the incorporation of four light-harvester units in the molecular cage.

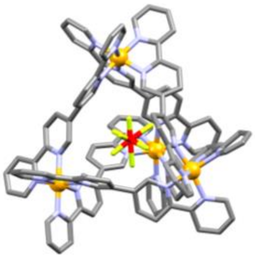

Figure 1. *X-ray molecular structure of the tetrahedral $[\mathrm{Cr^{III}}_4\mathrm{L}_6]^{12+}$ molecular cage (L = 2,2’:5’,5’’:2’’,2’’’-quaterpyridine) encapsulating a PF_6 anion.*

Acknowledgments.

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PP22

Synthesis and Encapsulation of Luminescent Triphenylene NHC Gold(I) Complexes

Anyie P. Atencio[1], Mounsef Lahboubi[2], Inmaculada Angurell[1], Joaõ Carlos Lima[3], Kristin Bartik[2], Laura Rodríguez[1]

[1]Department of Inorganic and Organic Chemistry, Universitat de Barcelona, Martí Franquès 1-11, 08028 Barcelona (Spain)

[2]Laboratoire de Chimie Organique, Université libre de Bruxelles (ULB), Avenue F.D. Roosevelt 50, CP160/06, B-1050 Brussels (Belgium)

[3]LAQV-REQUIMTE, Departamento de Química, Universidade Nova de Lisboa, Monte de Caparica (Portugal)

e-mail: aatences19@alumnes.ub.edu

In recent years, gold(I) N-heterocyclic carbene (Au^I–NHC) complexes have emerged in a wide variety of optoelectrical materials[1] due to the synergy of two factors: the possibility of tuning the electronic and luminescence properties through aurophilic Au...Au interactions and the carbenes structural characteristics that allow the modulation of both the steric and electronic properties[2,3]. The main chemical properties responsible of this can be their incredibly strong sigma donor capacity, and the fact that a broad range of different substituents can be attached to the nitrogen atoms. In a previous research, interesting results were obtained with alkynyl gold(I) complexes using triphenylene as a chromophore. It is known that the functionalization of the triphenylene core with chains containing different functional groups offers many opportunities to modulate the behavior of the system while conserving the tendency to columnar organization which opens the possibilities for π-stacking interactions[4].

It can be also possible to incorporate the gold(I) complexes into confined spaces, such as micelles. The resulting system will display new properties such as: i) solubility of gold complexes in aqueous media, which enhances their applications in biological sensors; ii) room-temperature phosphorescence (RTP) which mean that confinement suppresses the non-radiative decay process and consequently it is a feasible strategy to improve the phosphorescence emission of gold(I) complexes.

Taking all of this into consideration, in this work we present the synthesis of two different series of triphenylene gold(I) carbene complexes and a systematic study of their encapsulation and photophysical properties.

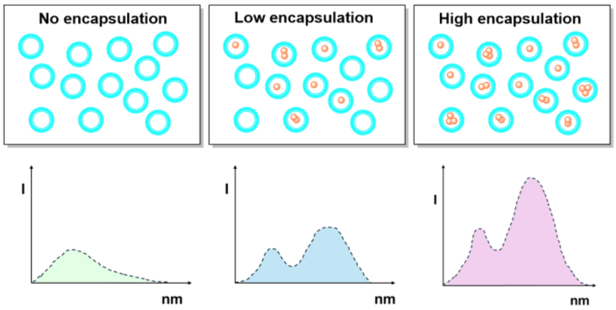

Figure 1. *Scheme of the effect of encapsulation on the fluorescence emission.*

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PP23

Study of T_n harvesting in gold(I) complexes

Araceli de Aquino[1], Artur Moro[2], João Carlos Lima[2], Laura Rodríguez[1]

[1] Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, E-08028, Barcelona, Spain

[2] LAQV-REQUIMTE, Departamento de Química, Universidade Nova de Lisboa, Monte de Caparica.

e-mail: aracelideaquino@ub.edu

Gold(I) complexes are known as promising candidates for the development of luminescent compounds[1]. The presence of this metal atom can induce the so-called *heavy atom effect* and, therefore, promote the *intersystem crossing transition*, which would be spin-forbidden[2], allowing the harvesting of T_n. The population of the triplet excited states is not trivial since many simultaneous mechanisms are in competition. In a first work, our group studied how to modulate the harvest of T_n by modification of the aurophilic contacts present in the compounds[3]. For that, two families of dinuclear gold(I) complexes have been prepared displaying intra- or intermolecular Au···Au contacts or also the lack of these contacts. The quantum yield of triplet excited state population, $\phi_{T,}$ has been calculated for all of them.

In a second work [4], different parameters have been studied relating their influence in the promotion of T_n. In this case, two families of mononuclear gold(I) compounds have been prepared, with three different chromophores displaying diverse electron-donor capabilities and two different phosphanes with different levels of bulkiness. Again, their ϕ_T have been calculated and studied. These experimental works have been supported with TD-DFT calculations to justify the trends observed and to fully understand the photophysical processes that take place.

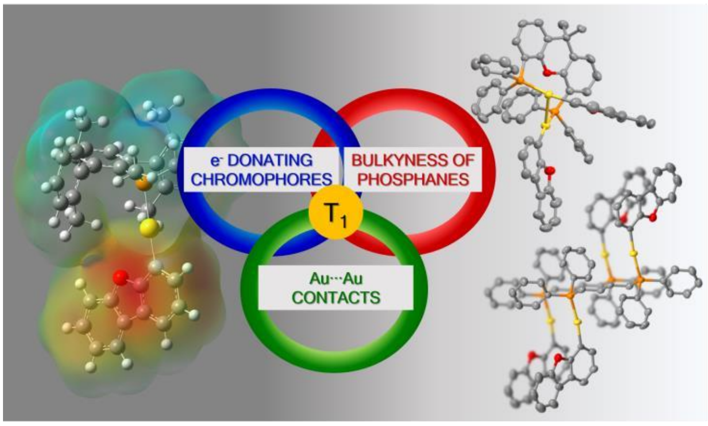

Figure. *Illustration of the different parameters studied for* ϕ_T.

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PP24

Etheno Adducts and CPD-like photoproducts: a new DNA photodamage

Carlos Montero-Galán[1*]; Paloma Lizondo-Aranda[1]; Gemma M. Rodríguez-Muñiz[1]; M.A. Miranda[1]; Virginie Lhiaubet-Vallet[1]

[1] Instituto de Tecnología Química, Universitat Politècnica de València- Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avd. de los Naranjos s/n, 46022 València, Spain

* *Email: cmongal1@itq.upv.es*

Lipid peroxidation is a biochemical process that involves the oxidation of polyunsaturated fatty acids, the components of cell membranes. In this process, highly reactive species, such as α,β-unsaturated aldehydes, are generated and react with DNA bases, forming the so-called **etheno adducts**. These DNA lesions exhibit **mutagenic properties** [1]. Indeed, the increase of lipid peroxidation in inflammatory processes [2] has been related to the high levels of etheno adducts in diseases that can lead to cancer, such as Chron's disease or ulcerative colitis[1]. Consequently, they are excellent **bio-markers** for different types of cancer (lung, colon or prostate cancer). Although their mutagenic properties have been clearly established, their photoreactivity has not been studied yet.

Here, the attention is centered on the cytosine etheno derivative (eC). Recently, the increase of its singlet excited state lifetime compared to that of cytosine was reported,[3] which points toward a **potentially higher reactivity**. Two model compounds containing two eC or eC and thymine covalently linked by a trimethylene bridge were synthesized and their photoreactivity was evaluated under **direct irradiation** or through a **photosensitization** process. Interestingly, under both conditions, a sole photoproduct, characterized as a cyclobutane pyrimidine dimer-like compound, was evidenced for the first time. As in the case of its cyclobutane pyrimidine dimer (CPD) analogue, formation of this lesion might arise from a **[2+2] photocycloaddition** involving the double bond at 5,6 of the thymine and eC. In addition, mechanistic insights were obtained from emission and transient absorption experiments.

Formation of edC already means a damage by itself, but its harmfulness could be increased if it can form a CPD-type photoproduct. Thus, the aim of this study is to evaluate the photoreactivity of these etheno adducts, considering especially the formation of new CPD-like lesions.

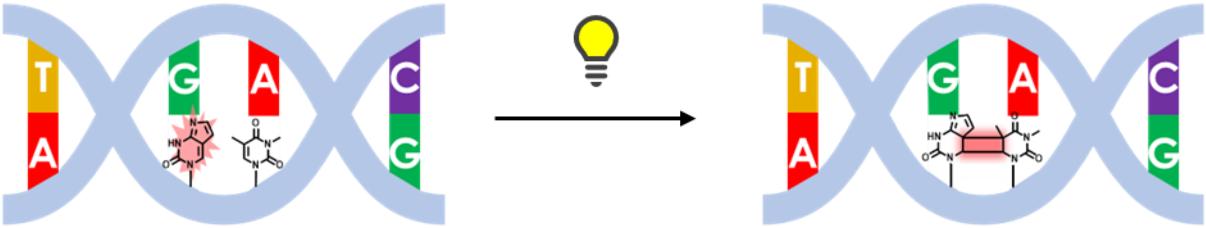

***Figure 1**: Graphical representation of the eC-T model and its CPD formation.*

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PP25

Cross-comparison of the photochromic and mechanical properties of azo nanoparticles and thin films

Federico Zizzi[1]*, Eléna Ishow[1], Stéphane Cuénot[2]

[1] CEISAM-UMR 6230, Nantes Université, 44322 Nantes, France

[2] IMN-UMR 6502, Nantes Université, 44322 Nantes, France

* *federico.zizzi@univ-nantes.fr*

Azo compounds, thanks to their reversible and selective E-Z photoisomerization reaction around their central N=N bond, have recently bolstered considerable interest in biology as they can alter physiological properties and trigger drug delivery through the remote control of light.[1] Until now, most studies have involved water-dispersible azo dyes, micelles or hydrogels but not at the nanoparticle level. In this context, mastering the morphology and elasticity of nanoparticles can exert, for example, tantamount effects on drug delivery process.[2] Among the vast range of possible nanoparticles, photochromic organic nanoparticles (PONs), exclusively based on self-assembled photochromes, have appeared as a new class of functional nanomaterials with a high payload of active units.[3] In this study, azo NPs have been fabricated through a flash nanoprecipitation method from a concentrated solution of dyes. To avoid issues relied to NP disassembly, we resorted to crosslinked architectures, incorporating crosslinkers with varying flexibility. Atomic Force Microscopy (AFM) investigations revealed marked differences in mechanical properties, particularly the elastic modulus, influenced by the linker flexibility. This trend was consistent in both photocrosslinked thin films and azo nanoparticles (NPs), yet the NPs exhibited notably higher elastic modulus values compared to that of thin films. Photochromic investigations of photocrosslinked azo NPs revealed a smaller E→Z photoconversion for PONs compared to that of pristine PONs probably due to the formation of a denser system, as revealed by TEM imaging (**Figure 1**).[5]

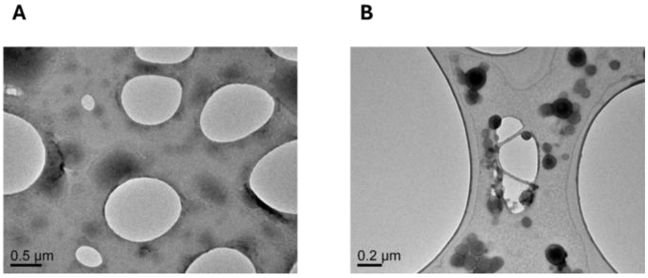

Figure 1. TEM images of azo PONs deposited on carbon grids. A) PONs before photo-irradiation; B) PONs after photo-irradiation.

As a prospect, cooperative systems studies are needed to enhance internal azo motion and overall macroscopic movement in photocrosslinked azo PONs.

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PP26

Tuning Singlet Oxygen Generation in Heavy-Atom-Free BODIPY Dyes via Boron and Carbon Substitution

Andrea Albaya[1]*, Larissa Maierhofer[1], Ruth Prieto[2], Teresa Arbeloa[2], Raúl Montero[2], Asier Longarte[2], Enrique Mann[1], Virginia Martínez-Martínez[2], Jose Luis Chiara[1]

[1]Institute of General Organic Chemistry, IQOG-CSIC, Madrid, Spain
[2]Faculty of Science and Technology, University of the Basque Country-EHU, Bilbao, Spain
**andrea.albaya@csic.es*

The heavy-atom effect is commonly used to enhance ISC efficiency and singlet oxygen ($^1O_2$) yield in photosensitizers by incorporating halogen or transition metal atoms with large atomic numbers into their structures. However, this strategy also enhances the ISC of $T_1 \rightarrow S_0$, leading to significantly shortened triplet lifetimes, along with inherent cytotoxicity and poor water solubility caused by the heavy atoms, which limit their applications. Compact BODIPY dyads containing mutually orthogonal donor and acceptor subunits are efficient photosensitizers that do not require the presence of heavy atoms.[1] In this case, triplets are generated via spin-orbit charge transfer intersystem crossing (SOCT-ISC).[2] In this work, we have studied the combined effects of chromophore alkylation and boron substitution on fluorescence emission, and ISC, and $^1O_2$ generation efficiencies in very simple and easily accessible BODIPY systems (see Figure). Alkyl substitution enhances fluorescence, whereas replacing fluorine atoms on boron with stronger electron-withdrawing groups enhances ISC and $^1O_2$ generation efficiencies, particularly in solvents of medium polarity. Our studies demonstrated that these structural modifications of simple phenyl-BODIPY donor-acceptor systems can significantly increase the quantum yield of singlet oxygen generation (up to 0.75), enhancing their potential applications in PDT, photocatalysis, and photovoltaic devices for efficient energy conversion.

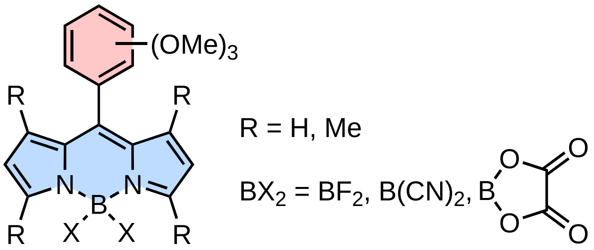

Figure. *Structures of BODIPYs studied in this work (donor: in red; acceptor: in blue).*

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PP27

Nanothermometry as a tool to study the hydration layer of charged nanoparticles

Ramon Raposo Filho[1]*, Fernando Maturi[1], Carlos Brites[1], Luís Dias Carlos[1]

[1]Phantom-g, CICECO- Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal

*Corresponding author: rraposofilho@ua.pt

Water behaves differently near charged interfaces, displaying a much lower dielectric constant when compared to bulk water[1], which can be controlled by the fine-tuning of the solution pH.[2]

A recent study by Maturi et al. explored this idea and showed that the structural fluctuations from LDL to HDL at the hydration layer of charged nanoparticles cease once the temperature is higher than its critical temperature (Tc), which in turn can be controlled by varying the surface charge of the NP. [3]

This effect and other strange properties of interfacial water molecules at a solid surface are crucial to understanding the role of water in heterogeneous reactions[4] as well as for the designing of optimal desalination membrane pores[5], where water shows an anomalous behavior as it increases its mobility when confined inside nanotubes, however, the understanding of how temperature affects the dynamic properties of confined water is still missing.[6]

Although not fully understood, the interplay between the LDL and HDL motifs appears to be one of the missing elements of this puzzle.[7] This will lead us to a fundamental understanding of the role of water in designing reaction systems (active sites and local environment) to mimic the action of enzymes in nature and to achieve higher rates and selectivities.[8]

Another important application of the knowledge of the structure of water is for attaining more efficient diagnostic and chemotherapeutic approaches, aiming at an improved prognosis for oncology patients.[9] This research was highlighted by the work of M.P. Marques et al., which showed that as the concentration of the antitumor drug increases the intramolecular H-bond network characteristic of intracellular water becomes more similar to the structure of LDA, low-density amorphous, ice.[10] Similar to the effect found for the Brownian velocity at the hydration layer of the UCNPs as the concentration of HCl was increased. Therefore, while the primary targets of drugs are biological receptors, they then propose water as a potential secondary target for chemotherapy.[11]

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PP28

Light and pH controlled DTE-CB8 rotaxanes in water

Miriam Colaço[1]*, A. Jorge Parola[1], Nuno Basílio[1]

[1]Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

* *mr.colaco@campus.fct.unl.pt*

Rotaxanes are important mechanically interlocked molecules that can be applied in molecular machines. Its formation is mostly based in bulky hydrophobic stoppers which can hamper the development of water-soluble rotaxanes. In this communication, we present high-affinity host-guest pairs in water, based on 1:1 complexes between a cucurbit[8]uril (CB8) host and photoswitchable dithienylethene (DTE) guests. We show[1,2] that the complexes with the colored ring-closed isomers are, about two orders of magnitude, thermically and kinetically more stable at than the ones of the fluorescent open forms, that can be obtained from the former by irradiation with biologically permeable near infrared light. Through the introduction of two sulfonate side arms in the DTE,[3] the light-responsive kinetic constants slow down by at least 5 orders of magnitude (figure), due to the electrostatic repulsion between these groups and the electronegative portals of CB8. Following this study, we developed a pH-controlled system with an even stronger electrostatic barrier towards the formation of rotaxanes and methods to easily obtain them *in situ*. Additionally, these DTE derivatives with electrostatic stoppers allow the observation and characterization of its CB8 complexes that appear in of out-of-equilibrium conditions. These present unusual three-dimensional arrangements and therefore exhibit different photochemical and affinity properties.

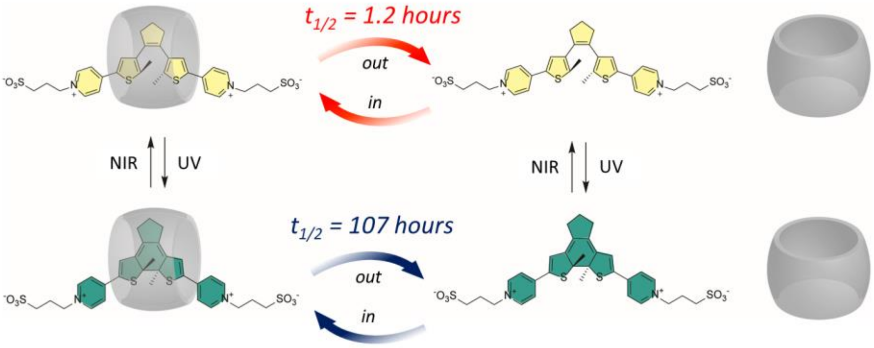

Figure. *Light control over the displacement kinetics of the 1:1 complexes that CB8 forms with the DTE guest.*[3]

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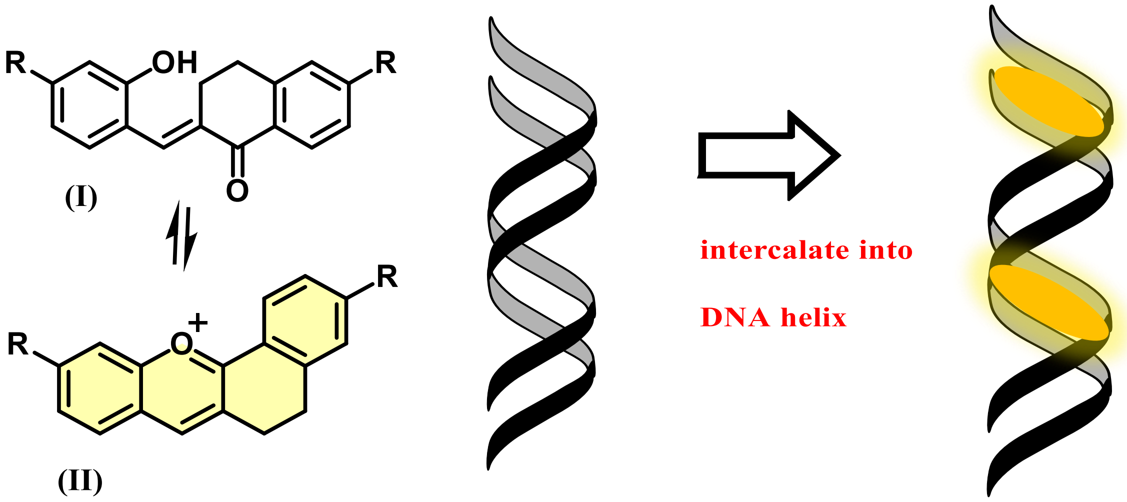
PP29

Exploring the Binding Properties of Flavylium Derivatives to ds-DNA

H. Mahmoodi*, A. J. Parola, N. Basílio
LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
* *h.mahmoodi@campus.fct.unl.pt*

Flavylium cations are renowned for their ability to establish supramolecular interactions with synthetic and natural receptors, being good candidates to bind nucleic acids, specifically DNA.[1] This study focused on exploring the binding affinities and modes of interaction between flavylium cations and DNA utilizing UV-VIS spectroscopic techniques. The switchable nature of the flavylium-chalcones system, coupled with its fluorescence properties and specific interactions with DNA, make it a promising candidate for various biochemical applications. The results support the notion that flavylium cations establish strong interactions with the DNA double helix.

Different flavylium derivatives have been synthesized and their interaction with calf thymus ds-DNA were investigated by UV-Vis spectroscopy in phosphate buffer at pH 7. Additionally, the influence of DNA on the flavylium-chalcone equilibrium was investigated in order to evaluate the potential of these compounds to develop stimuli-responsive small molecule DNA-binders for biological applications.



***Scheme1**: Interaction between flavylium and DNA. (I) trans-chalcone; (II) flavylium.*

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PP30

Photo- and pH-Responsive 2-Hydroxychalcone−β-Cyclodextrin Conjugate: A Study on Modulated Binding

Micael Paulino[1]*, Ignacio Pérez-Juste[2], María Magdalena Cid[2], José P. Da Silva[3], M. Manuela A. Pereira[1], Nuno Basílio[1]

[1] Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[2] Facultade de Química, Edificio de Ciencias Experimentais, Universidade de Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain

[3] Centre of Marine Sciences (CCMAR/CIMARLA), University of Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

* *md.paulino@campus.fct.unl.pt*

Cyclodextrins (CDs) are highly valued in supramolecular chemistry for their ability to encapsulate guest molecules within their hydrophobic cavities, making them indispensable in various industries and crucial for developing molecular machines and supramolecular polymers.[1] Flavylium salts, a diverse group of dyes, are studied for their multistate photoswitching properties, enabling light-responsive host-guest complexes with CDs.[2]

Herein, we present the design, synthesis, and detailed characterization of a stimuli-responsive 2hydroxychalcone−β-cyclodextrin conjugate (Figure 1).[3] The results show that the pendant 2-hydroxychalcone arm forms an intramolecular self-inclusion complex within the cyclodextrin cavity. These stimuli-responsive properties suggest potential applications in developing switchable functional materials.

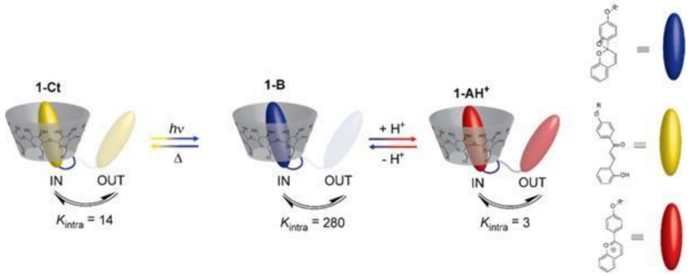

Figure 1 Control over the self-inclusion complex affinity through the trans-chalcone 1-Ct (Moderate Affinity)–Hemiketal 1-B (high Affinity) or Flavylium 1-AH+ (low affinity) interconversion using only light or light and pH stimuli, respectively.

Acknowledgments

This work was supported by the Associate Laboratory for Green Chemistry LAQV (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020), which is financed by national funds from FCT/MCTES. FCT/MCTES is also acknowledged for supporting the National Portuguese NMR Network (ROTEIRO/0031/2013-PINFRA/22161/2016, cofinanced by FEDER through COMPETE 2020, POCI, PORL, and FCT through PIDDAC) and for the projects UIDB/04326/2020 and PTDC/QUI-COL/32351/2017, and the PhD grant of M.P. (UI/BD/154489/2022). This study also received Portuguese national funds from the operational programs CRESC Algarve 2020 and COMPETE 2020 through project EMBRC.PT ALG-01-0145-FEDER-022121.

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PP31

Same goal, different perspectives: photocatalytic removal of pharmaceuticals by 2D/3D immobilized photocatalysts

Manuel Peñas-Garzón[1,2,*], Maria J. Sampaio[1,2], Cláudia G. Silva[1,2], Joaquim L. Faria[1,2]

[1]LSRE-LCM – Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[2]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

* *manuelpgarzon@fe.up.pt*

The potential implementation of heterogeneous photocatalysis (among the most representative advanced oxidation processes), for environmental applications is usually related to diverse challenges. These include the need to support the photocatalysts (semiconductor particles) to reduce, or even avoid, post-reaction recovery stages.[1] This work aims at evaluating the performance of graphitic carbon nitride (g-C_3N_4, here labeled as CN), a well-known photocatalyst active under visible irradiation based on a metal-free layered structure, immobilized on different 2D (film) and 3D (cylindrical) supports. The immobilized CN was tested in the removal of pharmaceuticals (including from antidepressants as venlafaxine to analgesics like tramadol), selected based on their potential impact on water ecosystems, using LED lights. Results confirmed the ability of the CN anchored to a cylindrical support to operate following modular-like systems, whereas the immobilization on a film demonstrated the satisfactory continuous treatment of pharmaceuticals (Figure 1) spiked in natural surface waters using planar reactor configurations. The simple set-and-use feature, the versatility of the systems used, and the outstanding photocatalytic performance demonstrated that the supported photocatalysts represent a promising approach for further environmental elimination of refractory contaminants in real surface waters.

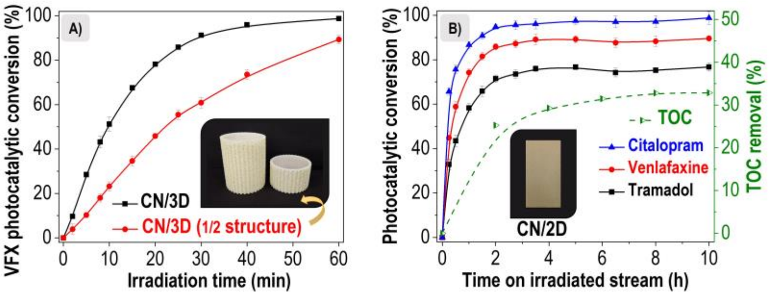

Figure 1. *A) Photocatalytic removal of venlafaxine (VFX) using CN anchored on the 3D (cylindrical) structure, and B) Continuous conversion of pharmaceuticals using the CN immobilized on the 2D (film) support.*

Acknowledgments

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PP32

Biomass-derived Carbon Dots as Fluorescence Lifetime Imaging Probes

María Rosell,[1] Verónica Torregrosa-Rivero,[2] Andrés Ruiz-Garzón,[1] Javier García-Martínez,[2] Diego Herrera-Ochoa,[1] Elena Serrano,[2] Cristina Martín[1]

[1] FOTOAIR, Dpto. Química-Física, Universidad de Castilla-La Mancha, Facultad de Farmacia. Av. Dr. Jose Maria Sánchez Ibáñez, S/n, 02071 Albacete (Spain)

[2] Laboratorio de Nanotecnología Molecular, Dpto. Química Inorgánica, Universidad de Alicante, Carretera Alicante-S. Vicente s/n, 03690 Alicante (Spain).

maria.rosell@uclm.es

The importance of early and accurate medical diagnosis is critical in a society where mortality rates and healthcare costs are rising. The use of light in medicine, and more specifically fluorescence techniques, has emerged as a sensitive alternative with unprecedented spatio-temporal resolution, allowing not only the measurement of small changes in biological processes but also the monitoring of the evolution of treatment in real time.

Among all of the advances in the development of superior inorganic and organic nanomaterials with outstanding physical and chemical properties as a fluorescent probe. Carbon dots (CDs) stand out because they can be prepared from inexpensive and abundant resources (polysaccharides and urea) using environmentally friendly processes (hydrothermal synthesis).

However, up to now, the lack of knowledge about the exact mechanism of CD formation, together with the poorly understood photophysical mechanism, has blocked the production of high-quality CDs with the desired properties. Therefore, this research unravels the structure-properties relationship where it was found that their optical properties are determined by the degree of graphitization of the carbonaceous core, while the surface groups allow to tune this emission, and both of which are determined by the structure of the precursor used as carbon source. Furthermore, the pH-sensitive fluorescence, combined with its long fluorescence lifetimes observed in living cells (> 10 ns), where they were found to be non-toxic and efficiently taken up by cells, positions these biomass-derived CDots as probes for time-resolved fluorescence imaging (FLIM).

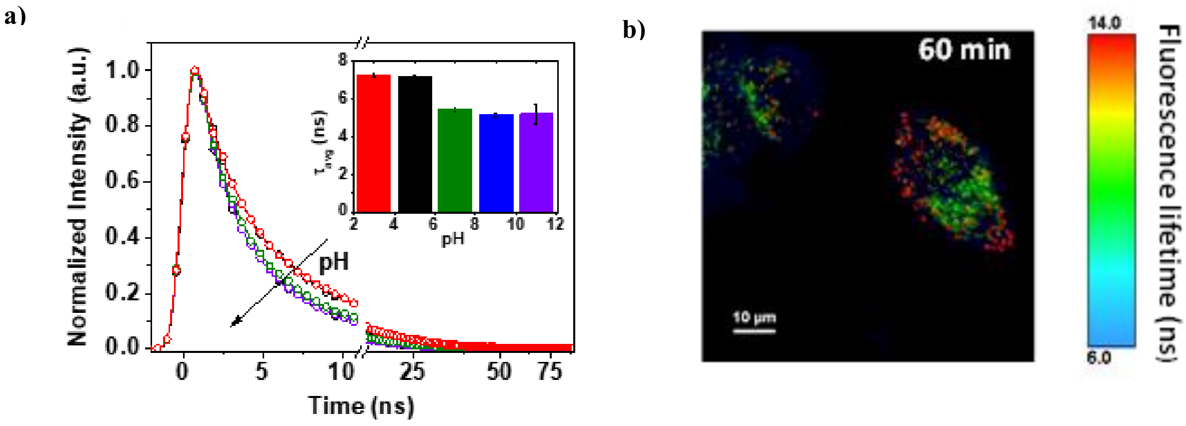

Figure 1*. a) Emission decays of CDCE at different pH upon excitation at 360 nm in water solution. The inset shows the average lifetimes analysis of the emission decays in the same pH range. b) FLIM images of MCF-7 cells treated with CDCE (0.25 mg/mL) after 60 min of incubation.*

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PP33

The Nature of Charge on Porphyrin Structure Unexpectedly Stimulates the Aggregation of the Photosensitizer at the Surface of the Human Serum Albumin

Otávio Augusto Chaves[1]*, Carlos Serpa[1]

[1]Department of Chemistry, Coimbra Chemistry Centre - Institute of Molecular Sciences (CQC-IMS), University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal.

*otavioaugustochaves@gmail.com

Porphyrins belong to a class of natural or synthetic organic heterocyclic widely studied in the medicinal chemistry field as photosensitizer for photodynamic therapy of cancer (PDT), photodynamic inactivation of microorganisms (PDI), and theranostic agents [1]. The non-charged 5,10,15,20-tetra(pyridine-4-yl)porphyrin (4-TPyP), positive charged tetra-cationic(4-pyridyl)porphyrin (4-MeTPyP), and negative charged 5,10,15,20-tetrakis(2,6-difluoro-3-sulfophenyl)porphyrin ($TDFPPS_4$) were reported as potential photosensitizer for PDT [2-4]. The ability of the photosensitizers to be carried in the human bloodstream is predominantly determined by their extension of binding mechanism and binding location to Human Serum Albumin (HSA), influencing their biodistribution and ultimately their PDT efficacy in vivo [5]. Thus, the present work reports a comparative study on the interaction between the HSA with 4-TPyP, 4-MeTPyP, and $TDFPPS_4$ via multiple spectroscopic techniques under physiological conditions, combined with in silico calculations. The nature of the charge in the porphyrin structure was also evaluated in terms of the binding capacity and mechanism to HSA.

Both UV-vis and steady-state fluorescence parameters indicated a ground state association between HSA and 4-TPyP or 4-MeTPyP and the absence of any dynamic fluorescence quenching was confirmed by the same average fluorescence lifetime for HSA without and with 4-TPyP or 4-MeTPyP ($\tau_o/\tau \approx 1.0$) [2,3]. Thus, the Stern–Volmer quenching (K_{SV}) constant reflects the binding affinity, indicating a weak to moderate interaction (10^3-10^4 M^{-1}), being spontaneous ($\Delta G < 0$), enthalpically and entropically driven [2.3]. On the other hand, the interaction HSA:$TDFPPS_4$ occurs via the combination of ground state association and collisional phenomenon with a binding constant (K_a) value in the order of 10^5 M^{-1}, indicating a strong binding affinity. Curiously, despite the porphyrin binding into an internal pocket (site I), about 50% of $TDFPPS_4$ structure is still accessible to the solvent, making aggregation in the bloodstream possible. This results in an adverse scenario for anionic porphyrins to achieve their therapeutical potential as photosensitizers and control of effective dosages. Overall, comparing the data of this work with those reported in literature, we identified a trend of anionic porphyrins to show the combination of fluorescence quenching mechanisms and to induce distinct interaction trend.

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PP34

Photoinduced Plasmon-assisted Functionalization of Gold Nanorods for Improved Plasmon-based Sensors

David Botequim [1], Rui Oliveira-Silva [2], Vanda V. Serra [1], Ana S. Viana [1], Peter Zijlstra [3], Duarte M. F. Prazeres [2], Sílvia M. B. Costa [1], Pedro M. R. Paulo [1]*

[1] Centro de Química Estrutural - Institute of Molecular Sciences, and [2] Institute for Bioengineering and Biosciences, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

[3] Institute for Complex Molecular Systems (ICMS), Eindhoven University of Technology, Eindhoven 5612 AZ, The Netherlands

* *pedro.m.paulo@tecnico.ulisboa.pt*

The strong interaction of gold nanoparticles with light, through collective oscillations of free electrons in the metal, has been explored in many ways to develop optical detection schemes for biochemical sensors. Generally, the detection scheme requires that target species interact with the particle's surface, which is accomplished by its modification with molecular recognition units. The motivation behind the development of regioselective functionalization strategies, as opposed to indiscriminate full surface coating, is based on a more rationale use of the particle's surface by directing the target species to its more sensitive regions (plasmon hot spots), while leaving other regions available for complementary functionalities, such as colloidal stabilization or anti-fouling coatings. The pursuit of such strategies has contributed to enhance single-molecule detection of proteins,[1] and to the development of brighter fluorescent nanoprobes.[2] Recently, we have explored a new photoinduced plasmon-assisted strategy to target hot spots in gold nanorods for modification with bioreceptor units. The biotin-functionalized gold nanorods respond specifically to streptavidin binding, thus, providing a model plasmonic biosensor with a total peak wavelength shift of ca. 4 nm (Fig. 1).

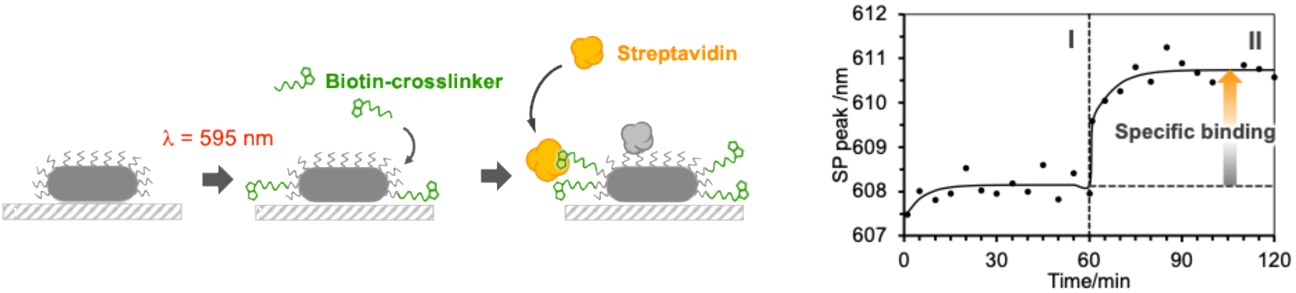

Figure 1. *(Left) Functionalization of gold nanorods with biotin receptors using irradiation at surface plasmon (SP) resonance wavelength. (Right) Surface plasmon peak shift in response to streptavidin (100 nM) in PBS buffer.*

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PP35

Pushing the Boundaries of Electron Transfer Reactions

Amílcar Duque-Prata*, Luis G. Arnaut, Carlos Serpa

CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535, Coimbra, Portugal
* *adp@uc.pt*

Electron transfer (ET) reactions are ubiquitous in our daily lives, playing crucial roles in processes such as respiration, photosynthesis, photovoltaic cells, and molecular electronics, among various other examples. An intramolecular electron transfer reaction can be considered the simplest chemical reaction, as it "only" involves the movement of an electron from a donor moiety to an acceptor one. In photoinduced ET reactions, the process is initiated by light, forming a locally excited state, which then evolves to a charge-separated state before returning to the ground state. Despite the apparent simplicity of an electron moving through a molecule, the theoretical description of ET reactions was subject to much debate. The award of the 1992 Nobel Prize in Chemistry to Rudolph Marcus reflects the current dominant understanding of the factors that control electron transfer rates, where solvent reorganization is believed to be the major contributor to the reaction barrier in polar solvents.

However, the fundamental mechanisms of ET reactions remain open to scrutiny, especially when dealing with highly exergonic reactions. In 2018,[1] it was experimentally demonstrated that Marcus inverted region, where the ET rate decreases with increasing exergonicity, does have an end. A double-inverted region, where the rate increases again for high-exergonic reactions, was observed in two organic donor-spacer-acceptor (D-S-A) systems in different non-polar solvents.

The investigation of ultra-exothermic ET is now extended to polar solvents. ET reactions in a D-S-A system in different alcohols, which lead to small variations in the charge-recombination Gibbs free energy, were studied using ultrafast time-resolved absorption spectroscopy. Significant changes were observed in the ET rate when changing the solvent. This behavior is even more evident when data from non-polar solvents is included. These observations suggest that established electron transfer theories should be revised to better describe the end of the Marcus inverted region and the existence of a new kind of behavior for extreme exergonic reactions.

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PP36

Unravelling Protein Folding Dynamics with Photoacoustic Calorimetry: the case of Chignolin

Amado D*, Chaves OA, Loureiro R, Jesus CS, Cruz PF, Almeida ZL, Serpa C, Brito RMM

CQC-IMS, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

* *samadodaniela2@gmail.com*

Background: Here, we studied the dynamics of chignolin, a short β-hairpin peptide that serves as a model for studying conformational changes in β-sheet proteins[1], since in depth characterization of fundamental folding steps in model peptides provides invaluable insights into the folding mechanisms of more complex biomolecules. Despite previous suggestions, the role of specific interactions, such as the Tyr2-Trp9 interaction, in chignolin's folding mechanism remained elusive. Through a multi-technique approach employing circular dichroism (CD), nuclear magnetic resonance (NMR), ultra-fast pH-jump coupled with TR-PAC, and molecular dynamics (MD) simulations, we unravel pH-dependent conformational changes in the peptide. Our findings unveil a comprehensive picture of chignolin's folding kinetics under local pH variations, emphasizing the importance of the Tyr2-Trp9 interaction in stabilizing the β-hairpin structure.

Methods: Experiments of laser-induced pH jump coupled with TR-PAC were accomplished using a homemade flow cell with temperature control and automatic injection. The PA pressure waves were detected using both 2.25 and 1 MHz frequency microphones. Analysis of these waves was performed with the CPAC software developed in our laboratory and available online (http://cpac.qui.uc.pt/)[2]. We carried out NMR, circular dichroism studies in the far-UV and MD simulations with the chignolin peptide.

Results and conclusions: Ultra-fast pH-jump TR-PAC experiments on chignolin determined its refolding kinetics from high pH, with a lifetime of 1.15 μs, consistent with prior studies[3]. TR-PAC, along with CD, NMR, and MD data, indicates that the protonated state of Tyr2 is crucial for chignolin’s stabilization. At high pH, Tyr2 deprotonation disrupts hydrophobic interactions with Trp9 and Pro4, leading to a disorganized peptide structure. A fast pH-jump triggers refolding, accompanied by a volume expansion of 10.4 mL mol-1. NMR and MD simulations show that at high pH, the aromatic rings of Trp9 and Tyr2 lose close interaction, resulting in a flexible structure. Protonation of Tyr2 re-establishes the hydrophobic core, forming intra-molecular hydrogen bonds and expelling water molecules. This hydrophobic collapse is key in β-hairpin peptide folding, as supported by Karplus and Dinner's theory[4].

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PP37

Making the Invisible Visible with new NIR emissive dyes for Fluorescence Image Guided Surgery

Maria João Álvaro Martins[1]*, Carlos Baleizão[1], José Paulo Farinha[1], Ermelinda M. S. Maçôas[1],

[1] *Centro de Química Estrutural (CQE) e Institute of Molecular Sciences (IMS), Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*

* *maria.a.martins@tecnico.ulisboa.pt*

Augmented reality platforms for 3D visualization based on fluorescence imaging are nowadays a reality in the operating room. Fluorescence Image Guided Surgery (FIGS) provides in situ, real-time visualization of solid tumors by labelling the malignant tissue with cancer targeted fluorescent probes. Compared to other imaging techniques (CT and MRI), fluorescence imaging is a simple and cost effective procedure that offers high contrast and sensitivity without disrupting the workflow during surgery. However, to make this procedure a standard of care for diagnosis and tumor resection, we need versatile tumor targeted fluorescent dyes emitting near-infrared light (NIR-I, 650-900 nm), able to provide high tumor to healthy tissue contrast for a broad range of tumors. Despite the very active research in fluorescent labels, only a handful of dyes have been approved for clinical use, the most popular being indocyanine green (ICG) used in nearly 60% of the clinical studies. Like most NIR organic dyes, ICG suffers from poor stability in biological media, low brightness,[1] lack of active tumor specificity and fast diffusion out of the tumor site. Such limitations can be partially circumvented by encapsulating the dyes in biocompatible nanocarriers. In this work we discuss the development of a dye for incorporation into a multifunctional NIR fluorescent nanolabel for FIGS.

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PP38

Doubling photoluminescence quantum yield : SF sensitizer for Lanthanides complexes

C. Ciambrone[1]*, C. Davies[1], A. Del Guerzo[1], A.T. Bui[1]

[1] Institut des Sciences Moléculaires UMR 5255 CNRS / Université de Bordeaux, 33405, Talence, France
* Email address: charles.ciambrone@u-bordeaux.fr

Lanthanide(III) ion-based complexes are characterized by their prolonged emission lifetimes and sharp emission bands, which are a result of the 4f-4f transitions occurring within shielded orbitals[1]. The influence of the nature of the ligands and the geometry of the complex, and surrounding environment on these orbitals is small, resulting in unique emission profiles for each Ln^{3+} ion. A significant challenge in leveraging the luminescence of lanthanides is the inefficiency of direct excitation that results in the use of ligands that exhibit favorable absorption characteristics, facilitating a stepwise sensitization process. Upon photon absorption, the ligand—acting as an antenna—transfers its energy to the lanthanide's metal core, triggering emission. Enhancing the efficiency of this energy transfer is essential to improve the luminescence quantum yield and overall brightness. This enhancement necessitates the creation and synthesis of custom organic antennas. In this context, we will explore the potential of these antennas to leverage photophysical properties such as singlet fission (SF). SF-capable antennas have the ability to transform a single absorbed photon into two triplet excitons, potentially doubling the maximum quantum yield[2]. The development of novel ligands[3] and the investigation of the photophysical characteristics of the resultant molecules will be detailed.

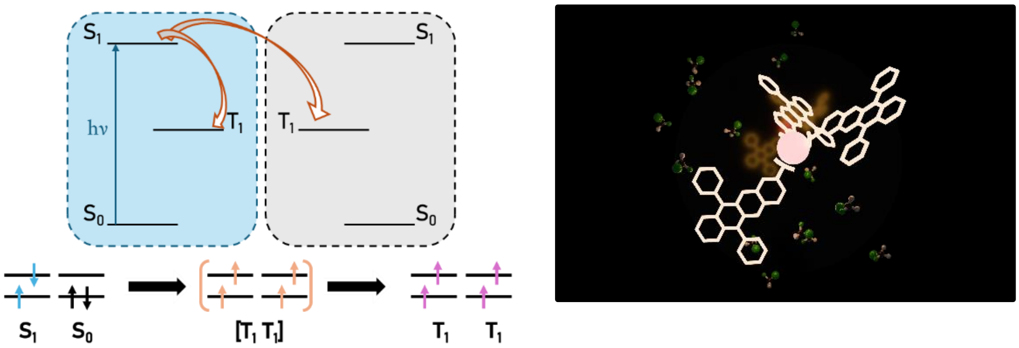

Figure. *a) simplified Jablonsky-Perrin diagram and schematic representation of singlet-fission process; b) schematic representation of target lanthanide complex.*

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PP39

Combination of photo-Fenton and electric current for the treatment of carbamazepine in continuous mode

Antón Puga[1,2]*, Cristina Soares[1], Marta M. Pazos[2], M. Ángeles Sanromán[2], Cristina Delerue-Matos[1]

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal

[2] Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

[3] CINTECX, University of Vigo, BIOSUV Group, Department of Chemical Engineering, Campus Lagoas-Marcosende, 36310, Vigo, Spain

** E-mail: anton.pazo@graq.isep.ipp.pt*

In this work, the degradation of the antidepressant carbamazepine (CBZ) through advanced oxidation processes (AOPs) has been investigated. The Fenton technique has been used through different ways of generating hydroxyl radical, highlighting the photo-Fenton and the electro-Fenton treatments. Both processes has been carried out with particles manufactured in the laboratory (acting as heterogeneous catalysts), composed of perovskite, carbon black and PTFE, whose detailed description is found in a previous work [1]. In this way, the catalyst has been used under the effect of ultraviolet light, with remarkable results. Afterwards, the application of electric current has facilitated the degradation, so the two techniques have finally been combined, in the so-called photo-electro-Fenton process, achieving eliminations of CBZ above 90%. Furthermore, seeking an approach beyond the laboratory scale, the experimental configuration proposed in this work has been tested in continuous treatment and with different wastewater matrices, simulating the flow of a wastewater treatment plant (WWTP) and a possible quaternary treatment, as an alternative to the lack of effectiveness of current WWTPs against micropollutants such as pharmaceuticals compounds.

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