PROGRAM 6JIF

6 JIF
Jornadas Ibéricas de Fotoquímica
11- 14 de Setembro, 2018 Aveiro

http://6jif.eventos.chemistry.pt/

Grupo de Fotoquímica da Sociedade Portuguesa de Química
Grupo Especializado de Fotoquímica de la Real Sociedad Española de Química
Universidade de Aveiro/Universidade de Coimbra

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This book summarizes the conferences and communications that will be presented at the VI Jornadas Ibéricos de Fotoquímica (6'JIF), Aveiro, 11-14 September 2018). The event is organized in the spirit of previous meetings (Santigo de Compostela in 2003; Faro in 2007; Granada in 2011, Lisbon in 2014, and Toledo in 2016), to bring together the Portuguese and Spanish Photochemistry communities into a high quality scientific program that spans over the many aspects of photochemistry and its interface with photophysics and photobiology, covering new and established techniques and methodologies, fundamental aspects, materials and applications.

The abstracts presented in this book illustrate well the high level achieved by photochemical/photophysical research in Portugal and Spain. The high number of communications and the diversity of themes presented show the vitality and progressive interest in the light-related sciences, from the traditional fields of photophysics, photochemistry and photobiology, to the interdisciplinary more recent fields of nanotechnologies, energy and environment. The large number of participants in this conference (100), mainly from Spain and Portugal, as well as the large number of authors from several countries, is a good proof of the growing development of photochemical/photophysical in Portugal and Spain and of its great internationalization.

The organizing committee has the honour to welcome all participants in this conference and wish them a productive stay in Aveiro thanking them for their valuable contributions to the scientific program. Aveiro is a charming and historical coastal city in the centre of Portugal, quite unlike any other, next to the sea and the ria (estuary) and crossed by a network of channels through which moliceiros (local boats) meander. This a place where urban sophistication and modernity meet and merge. With its University, constructed in 1973 and considered one of the youngest and most innovative and dynamic of the universities in Portugal, it is indeed a perfect scenario to promote fruitful scientific discussions during the meeting and foster the ties within our community. Our thanks also extend to all the people, entities and companies that collaborated in the organization of the event.

Luís D. Carlos and Sérgio Seixas de Melo

Program

Tuesday September 11, 2018

09:00 – 17:00 h **SALA DE ACTOS ACADÉMICOS – RECTORY BUILDING**

Chairs: Sérgio Seixas de Melo and Rute Ferreira

Training School on the basics of Photochemical, Photophysical and Photobiological Processes

http://academia.web.ua.pt/extraSCIRP/espacos/?t=1&id=10

09:00 – 10:30 h

Manuel Prieto

Centro Química-Física Molecular, IST, Universidade de Lisboa, Portugal
"Principles of Fluorescence and Energy Transfer (FRET) Methodologies"

COFFEE BREAK

10:30 – 10:45 h **HALL OF RECTORY BUILDING**

10:45 – 12:15 h

Luis Manuel Frutos Gaite

Unidad Docente de Química Física, Universidad de Alcala, Madrid, Spain
"Theoretical Photochemistry"

LUNCH

12:15 – 13:30 h **UNIVERSITY'S RESTAURANT**

13:35 – 15:00 h

José Manuel Gaspar Martinho

Centro de Química-Física Molecular, IST, Universidade de Lisboa, Portugal
"Two-photon absorption, imaging and sensing"

15:00 – 16:30 h

Wajih Al-Soufi

Universidad de Santiago de Compostela, Spain
"Supramolecular association studied by fluorescence spectroscopy"
(emphasis on Single Molecule Fluorescence and Fluorescence Correlation Spectroscopy)

16:30 – 17:00 h **INTERACTION WITH STUDENTS**

18:00 – 19:00 h **HALL OF RECTORY BUILDING**

REGISTRATION

19:00 h **RECEPTION**

SANTA JOANA MUSEUM

Wednesday September 12, 2018

09:00 – 18:30 h **SALA DE ACTOS ACADÉMICOS – RECTORY BUILDING**

http://academia.web.ua.pt/extraSCIRP/espacos/?t=1&id=10

08:00 – 18:00 h **HALL OF RECTORY BUILDING**

REGISTRATION

08:40 – 09:00 h **SALA DE ACTOS ACADÉMICOS – RECTORY BUILDING**

Opening ceremony, welcome addresses by Prof. Luís Carlos, Prof. Artur Silva, Vice-rector University of Aveiro and President of the SPQ and Prof. Sérgio Seixas de Melo

SESSION I *Chair*: Luís Manuel Frutos Gaite

09:00 – 10:00 h **PLENARY LECTURE**

Mario Nuno Berberan e Santos

Centro de Química-Física Molecular, IST, Universidade de Lisboa, Portugal

"Developments in thermally activated delayed fluorescence"

10:00 – 10:30 h **KEYNOTE LECTURE**

Juan Casado Cordón

Department of Physical Chemistry, Universidad de Malaga, Spain

"Diradicals: Structure and spectroscopy"

COFFEE BREAK AND POSTER SESSION

10:30 – 11:00 h **SENADO ROOM – RECTORY BUILDING**

SESSION II *Chairs*: Sérgio Seixas de Melo and Rachel Evans

11:00 – 11:20 h **INVITED LECTURE**

Julia Pérez Prieto

Instituto de Ciencia Molecular, Universidad de Valencia, Spain

"Exceptional optical features of lead halide perovskites"

11:20 – 11:35 h **ORAL COMMUNICATION**

A. J. Moro, L. Rodriguez, J. C. Lima

"Naphthyridine-based Gold(I) complexes: new tools for nucleotide sensing using aggregation induced emission"

11:35 – 11:50 h **ORAL COMMUNICATION**

B.Casteleiro, T. Ribeiro, J. M. G. Martinho, J. P.S. Farinha

"Hybrid gold nanoclusters-polymer nanoparticles as fluorescent probes"

11:50 – 12:05 h **ORAL COMMUNICATION**

P. M. R. Paulo, S. M. B. Costa, D. Botequim, R. Oliveira-Silva, D. M. F. Prazeres, A. P. Francisco, C. A. T. Laia, J. P. Conde

"Anisotropic gold nanoantennas for enhancing fluorescence detection: From single to dimer nanoparticles"

12:05 – 12:20 h **ORAL COMMUNICATION**

G. Orellana, A. B. Descalzo, J. Q. Alburquerque

"Sensing 1,3-dicarbonyl toxins with luminescent ruthenium(II)-polypyridyl complexes"

12:20 – 12:35 h **ORAL COMMUNICATION**

Biju Francis, Mariela M. Nolasco, Paula Brandão, Rute A. S. Ferreira, Luís D. Carlos

"Eu^{3+}-complex-based hybrid materials for luminescent solar concentrators"

LUNCH

12:45 – 14:00 h **UNIVERSITY’S RESTAURANT**

SESSION III *Chairs*: Hugh Burrows and Juan Casado Cordón

14:00 – 15:00 h **PLENARY LECTURE**

Rachel Evans

Department of Materials Science & Metallurgy, University of Cambridge, UK

“Spectral conversion materials to harvest sunlight in the urban landscape”

15:00 – 15:30 h **KEYNOTE LECTURE**

José Paulo Farinha

Departmento de Engenharia Química, IST, Universidade de Lisboa, Portugal

“Bright and stable nanomaterials for imaging and diagnostics”

15:30 – 15:50 h **INVITED LECTURE**

Francisco Galindo

Departamento de Química Inorgánica y Orgánica, Universitat Jaume I de Castellón, Spain

“Photoactive nanoclusters embedded in self-assembled fibrillar networks”

15:50 – 16:10 h **INVITED LECTURE**

Carlos Serpa

Departmento de Engenharia Química, Universidade de Coimbra, Portugal

“Piezophotonics”

16:10 – 16:25h **ORAL COMMUNICATION**

I. F. A. Mariz, E. M. S. Maçôas, J. M. G. Martinho, C. Santos, C. Correia

“On the origin of the emission of carbon nanodots: molecule-like fluorophores vs nanographene-like clusters”

COFFEE BREAK AND POSTER SESSION

16:30 – 17:30 h **SENADO ROOM – RECTORY BUILDING**

SESSION IV *Chair*: Manuel Prieto

17:30 – 17:50 h **INVITED LECTURE**

João Carlos Lima

Departamento de Química, Universidade Nova de Lisboa, Portugal

“Gold(I) complexes self-assembly, luminescence and applications”

17:50 – 18:10 h **INVITED LECTURE**

Mario Gutierrez Tovar

Universidad de Castilla La Mancha, Spain

“Luminescent Zr-Based MOFs: From Fundamental to LED application”

18:10 – 18:30 h **INVITED LECTURE**

Joaquim Faria

Departmento de Engenharia Química, Universidade do Porto, Portugal

“Shining new light on ancient formulations: preparation and photoproperties of graphitic carbon nitrides”

18:30 – 19:30 h **GRUFO-RSEQ/GFQ-SPQ Meeting**

Thursday September 13, 2018

09:00 – 18:10 h **SALA DE ACTOS ACADÉMICOS – RECTORY BUILDING**

http://academia.web.ua.pt/extraSCIRP/espacos/?t=1&id=10

SESSION V *Chair*: Gaspar Martinho

09:00 – 10:00 h **PLENARY LECTURE**

Juan Penedo-Esteiro

Laboratory for Biophysics and Biomolecular Dynamics, University of St. Andrews, UK

“Single-molecule photophysics of conjugated polymers in solution”

10:00 – 10:30 h **KEYNOTE LECTURE**

António Jorge Dias Parola

Departmento de Química, Universidade Nova de Lisboa, Portugal

“Photochromic supramolecular host-guest systems”

COFFEE BREAK AND POSTER SESSION

10:30 – 11:00 h **SENADO ROOM – RECTORY BUILDING**

SESSION VI *Chairs*: Juan Penedo-Esteiro and José Paulo Farinha

11:00 – 11:20 h **INVITED LECTURE**

Carlos Baleizão

Centro de Química-Física Molecular, IST, Universidade de Lisboa, Portugal

“Perylenediimides as building blocks for functional nanomaterials”

11:20 – 11:35 h **ORAL COMMUNICATION**

M. L. Renart, A. Coutinho, J. A. Poveda, M. Giudici, A. Fedorov, M. Berberan-Santos, J. Gonzalez-Ros, M. Prieto

“The membrane potassium channel KcsA - Exact analytical solutions for advanced homo-FRET to retrieve structural information”

11:35 – 11:50 h **ORAL COMMUNICATION**

C. M. Nunes, I. Reva, R. Fausto

“Photochemistry of aryl nitrenes: Doorway to elusive intermediates and tunnelling reactions”

11:50 – 12:05 h **ORAL COMMUNICATION**

A. M. Melo, J. Coraor, G. Alpha-Cobb, S. Elbaum-Garfinkle, E. Rhoades

“Determining a topological model for tau bound to tubulin heterodimers by SMFRET: Insights into its function/dysfunction”

12:05 – 12:20 h **ORAL COMMUNICATION**

Diego Sampedro

“Photoprotection: insights from theory and experiment”

12:20 – 12:35 h **ORAL COMMUNICATION**

C. S. H. Jesus, C. Serpa, R. Quintã, H. T. Soares

“Autofluorescence of protein aggregates enable in-vitro screening of anti-amyloid drugs”

LUNCH

12:45 – 14:00 h **UNIVERSITY’S RESTAURANT**

SESSION VII *Chairs*: Mario Nuno Berberan e Santos and Julia Pérez Prieto

14:00 – 14:30 h **KEYNOTE LECTURE**

Virginia Martínez Martínez
Departamento de Química Física, Universidad del País Vasco, Spain
"Fluorescent dyes into 1D-zeolitic materials for optical applications"

14:30 – 15:00 h **KEYNOTE LECTURE**

Carlos Lodeiro Espiño
Departmento de Química, Universidade Nova de Lisboa, Portugal
"Chalcogenide chemistry applied in the synthesis of nobel nanomaterials: the role of light and water"

15:00 – 15:20 h **INVITED LECTURE**

Elisabete M. S. Castanheira
Departmento de Física, Universidade do Minho, Portugal
"Magnetoliposomes as nanocarriers for fluorescent potential antitumor drugs"

15:20 – 15:35 h **ORAL COMMUNICATION**

A. Orte, <u>J. A. González-Vera</u>, F. J. Fueyo-González, Á. Ruiz-Arias, M. Morris, R. Herranz
"Quinolimide-based solvatochromic fluorophores"

15:35 – 15:50 h **ORAL COMMUNICATION**

<u>D. R. Ramos</u>, O. N. H. Kaabeche, M. Iazykov, J. A. Santaballa, R. Zouaghi, M. Canle
"Photodegradation of ionic liquids: Relevant aspects concerning photocatalyst activity"

COFFEE BREAK AND POSTER SESSION

15:50 – 17:30 h **SENADO ROOM – RECTORY BUILDING**

SESSION VIII *Chair*: Luis Manuel Frutos Gaite

2017 & 2018 winners of the best PhD thesis in photochemistry of the GRUFO

17:30 – 17:50 h **INVITED LECTURE**

Fabio Julia
School of Chemistry, University of Manchester, UK
"Photophysical and photochemical properties of cyclometalated platinum(II) and platinum(IV) complexes"

17:50 – 18:10 h **INVITED LECTURE**

Laura Francés-Soriano
Institut de Biologie Intégrative de la Cellule, CNRS, France
"NIR-responsive nanohybrids for efficient energy transfer"

18:45 – 20:15h **MOLICEIRO SIGHTSEEING TRIP**

20:30 h **CONFERENCE DINNER: RESTAURANTE OLARIA**

Friday September 14, 2018

09:00 – 13:00 h **SALA DE ACTOS ACADÉMICOS – RECTORY BUILDING**

http://academia.web.ua.pt/extraSCIRP/espacos/?t=1&id=10

SESSION IX *Chair*: Wajih Al-Soufi

09:00 – 10:00 h **PLENARY LECTURE**

Luis Arnaut

Departamento de Química, Universidade de Coimbra, Portugal

"From Photochemistry to Photomedicine: Health Solutions from Fundamental Science"

10:00 – 10:30 h **KEYNOTE LECTURE**

Uwe Pischel

Center for Research in Sustainable Chemistry, Universidad de Huelva, Spain

"Molecular engineering of two-photon absorbing four-coordinate organoboron fluorophores"

COFFEE BREAK

10:30 – 11:00 h **HALL OF RECTORY BUILDING**

SESSION X *Chairs*: Virginia Martínez Martínez and Uwe Pischel

11:00 – 11:20 h **INVITED LECTURE**

Ángela Sastre Santos

Instituto de Bioingeniería, Universidad Miguel Hernández, Elsche, Spain

"Photophysical and synthesis of fused-phthalocyanine systems"

11:20 – 11:35 h **ORAL COMMUNICATION**

E. Aguiló, R. Gavara, A. Moro, J. C. Lima, L. Rodriguez

"Tuning luminescence properties and morphologies in Au(I) supramolecular structures"

11:35 – 11:50 h **ORAL COMMUNICATION**

M. Novo, W. Al-Soufi, L. Piñeiro

"DNA intercalators studied by single-molecule fluorescence techniques"

11:50 – 12:05 h **ORAL COMMUNICATION**

E. Perez-Inestrosa, D. Collado Martín, Y. Vida, F. Najera, V. Stamenkovic

"Aminonaphthalimide-squaraine DYADS: Photophysical properties and bioimaging application"

12:05 – 12:20 h **ORAL COMMUNICATION**

R. Prieto-Montero, I. Lopez-Arbeloa, S. Lacombe, V. Martinez-Martinez

"Dye/silica nanoparticules for biomedical applications"

12:20 – 12:35 h **ORAL COMMUNICATION**

L. M. Frutos, M. Marazzi

"Tuning spectroscopic and photoreactivity properties of optical switches by external forces"

12:35 h **CLOSING**

PLENARY LECTURES

Developments in Thermally Activated Fluorescence

Tiago Palmeira, Érica Torres, Bruno Pedras, João Avó, Mário Berberan-Santos

CQFM and IBB, Instituto Superior Tecnico, Universidade de Lisboa, Portugal

Thermally Activated Delayed Fluorescence (TADF) has a unique temperature dependence and a duration typical of phosphorescence. There was a recent surge of interest in TADF owing to its application in 3rd generation Organic Light-Emitting Diodes (OLEDs) [1-3]. The basis of TADF is discussed, contrasting TADF in photoluminescence and TADF in electroluminescence [4-7]. Two different types of TADF are identified: One-way and two-way TADF [6]. It is shown that for a given efficiency, one-way TADF allows lower rates of reverse intersystem crossing. Graphical and quantitative indicators of singlet-triplet interconversion and photophysical efficiency are obtained and applied to the photoluminescence of several compounds and to the electroluminescence of TADF emitters specifically designed for OLEDs. Current developments in TADF OLED materials will also be discussed.

[1] Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronics. *Adv. Mater.* **2014**, *26*, 7931-7958.

[2] Shizu, K.; Lee, J.; Tanaka, H.; Nomura, H.; Yasuda, T.; Kaji, H.; Adachi, C. Highly Efficient Electroluminescence from Purely Organic Donor-Acceptor Systems. *Pure Appl. Chem.* **2015**, *87*, 627-638.

[3] Bergmann, L.; Zink, D. M.; Bräse, S.; Baumann, T.; Volz, D. Metal-Organic and Organic TADF-Materials: Status, Challenges and Characterization. *Top. Curr. Chem (Z)* **2016**, *374:22*.

[4] Dias, F. B.; Santos, J.; Graves, D. R.; Data, P.; Nobuyasu, R. S.; Fox, M. A.; Batsanov, A. S.; Palmeira,T.; Berberan-Santos, M. N.; Bryce, M. R.; Monkman, A. P., The Role of Local Triplet Excited States and D-A Relative Orientation in Thermally Activated Delayed Fluorescence: Photophysics and Devices, *Adv. Sci.* **2016**, 1600080.

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[6] Palmeira, T; Berberan-Santos, M. N. Kinetic criteria for optimal thermally activated delayed fluorescence (TADF) in photoluminescence and in electroluminescence, *J. Phys. Chem. C* **2017**, *121*, 701-708.

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SPECTRAL CONVERSION MATERIALS TO HARVEST SUNLIGHT IN THE URBAN LANDSCAPE

Ilaria Meazzini,[a] Niamh Willis-Fox,[a] Adarsh Kaniyoor,[a] Barry McKenna,[a] Guan Peng Lyu,[b] James Kendall,[b]
Trystan M. Watson,[c] and Rachel C. Evans[b]

[a] School of Chemistry, Trinity College Dublin, Dublin 2, Ireland
[b] Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, U.K.
[c] SPECIFIC, College of Engineering, Swansea University, Bay Campus, Swansea, SA1 8EN, U.K.

Single junction photovoltaic devices exhibit a bottleneck in their efficiency due to incomplete or inefficient harvesting of photons in the low- or high-energy regions of the solar spectrum. This can be overcome through the retro-fitting of a spectral converter to the device, which is used to convert solar photons into energies that are more effectively captured by the solar cell through a photoluminescence process.[1] However, while a lumophore may show seemingly ideal optical characteristics for spectral conversion in an ideal solution (high emission quantum yield, strong absorption), disappointment frequently awaits on its translation to the solid-state, where aggregation and quenching effects lead to significantly reduced photoluminescence yields.

In an effort to overcome this limitation, our research focusses on the bottom-up design of integrated lumophore-host materials for solar spectral converters, in which materials chemistry design strategies are used to control the packing, orientation and placement of π-conjugated lumophores in solid-state host materials. Since the electronic properties depend explicitly on the arrangement and packing of the π-conjugated species, this approach provides a means of modulating the optical properties. In this talk, we will report our recent results on the design of π-conjugated composite materials that utilise a family of organic-inorganic hybrid polymers known as the *ureasils* as the host.[2] Ureasils are comprised of a siliceous skeleton that is chemically-grafted to poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO) chains through urea cross-linkages, the number of which depends on the degree of branching in the organic polymer precursor. Ureasils are intrinsically photoluminescent,[3] exhibit high refractive indices and function as optical waveguides.[4] Through judicious selection of the degree of branching and length of the organic backbone and the incorporation method (grafting *vs* immobilization *vs* permeation), we can control the packing, orientation and placement of the π-conjugated species in the ureasil host. This in turn provides a means of modulating the optical properties. For example, a dramatic enhancement in the emission quantum yield to >60% is observed due to exciton localization at isolated nanodomains of a conjugated polyelectrolyte entrapped within the ureasil host.[5] Similarly, Förster resonance energy transfer from the ureasil to embedded or grafted conjugated lumophores can be exploited to tune the emission color[6,7] and even obtain white-light emission.[8] These characteristics can be exploited to improve light-harvesting and trapping within the integrated material, which can be used to develop highly efficient spectral converters to enhance the performance of solar cells.[9]

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[3] L. D. Carlos, R. A. S. Ferreira, R. N. Pereira, M. Assunção and V. de Zea Bermudez, *J. Phys. Chem. B* **2004**, 108, 14924.
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[9] A. Kaniyoor, B. McKenna, S. Comby and R. C. Evans, *Adv. Opt. Mater*. **2016**, *4*, 444.

Single-molecule photophysics of conjugated polymers in solution

F. Tenopala-Carmona[1], A. Brenlla[1], S. Fronk[2], G. Bazan[2], O. Kanibolotskyy[3], P. Skabara[3], I. D. W. Samuel[1] and C. Penedo[1]

[1]University of St Andrews, SUPA School of Physics and Astronomy, North Haug, KY16 9SS, St Andrews, Fife, United Kingdom
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[3]University of Strathclyde, Department of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

Conjugated polymers are an important class of organic semiconductors which combine novel optoelectronic properties with simple fabrication from solution and with many applications in a whole range of polymer optoelectronic devices – displays, solar cells, photodiodes and lasers. Remarkably the active layer of all these devices is deposited from solution by simple processes such as spin-coating or ink jet printing and, in recent years, it has become clear that the lack of knowledge regarding the conformation (shape) of conjugated polymers in relevant solution-processing conditions and how this influences their optoelectronic properties is hampering our progress towards more efficient devices and materials.

Since the first studies on conjugated polymers at single-molecule level, the use of these microscopy techniques in polymer science has experienced a stunning growth and most of these studies have focused on exploring polymer conformation using dilute solid solutions of conjugated polymers in a host matrix. However, this environment does not represent relevant solution-processing or polymer film conditions. In this talk we will describe our efforts to develop single-molecule spectroscopic techniques to investigate the impact of polymer conformation on light emission in organic solvents relevant for polymer processing. We will explore the chemical approaches we are using to incorporate end groups for specific polymer attachment to surfaces and nanoparticles and we will describe the characterization of P3HT and PFO polymers in different solvent conditions and how this impact polymer conformation and light emission.

FROM PHOTOCHEMISTRY TO PHOTOMEDICINE: HEALTH SOLUTIONS FROM FUNDAMENTAL SCIENCE

Luis G. Arnaut*

Chemistry Department, University of Coimbra, Portugal, lgarnaut@ci.uc.pt

In a society with an ever-increasing pace of change, science is requested to deliver fast solutions to old and new problems. In this context, there is a shift from science as the human endeavor to expand knowledge, to science as a tool to use existing knowledge to find solutions. Acknowledging the tension between these conflicting views of science, we present two examples of how fundamental science led to innovative health solutions.

The first example refers to Photodynamic Therapy (PDT) of cancer. [1] The design of new photosensitizers suggested innovative synthesis [2] that ultimately lead to molecules with nearly ideal properties for PDT.[3,4] One of these photosensitizers, named redaporfin, is currently in clinical trials for advanced head and neck cancer. Redaporfin already proved to be well tolerated and the predicted therapeutic effect was clinically observed. The stimulation of the immune system with redaporfin-PDT holds the promise of a systemic treatment for cancer.[5]

The other example concerns the non-invasive dermal delivery of large molecules. The photoacoustic effect suggested methods to generate high-intensity, high-frequency ultrasound pulses.[6,7] Such ultrasound pulses were found to transiently perturb the outer layers of the skin and increase its permeability to drugs.[8] Applications of the photoacoustic skin permeation are now commercially available in the dermocosmetics market.[9] The photoacoustic effect was also found to permeate the cell membrane and promote the transfection of genes. High-intensity, high-frequency ultrasound pulses are in the way to become a non-invasive and broad scope gene therapy method.

A satisfactory balance between a foundational and a utilitarian science is probably not achievable. However, in times of pressure for results, it is important to voice the role of science in the observation and conceptualization of phenomena in the physical world. In the words of Louis Pasteur: ""*la théorie seule fait surgir et développe l'esprit d'invention (…) dans les champs de l'observation le hasard ne favorise que les esprits préparés".*[10]

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KEYNOTE LECTURES

Diradicals: Structure and Spectroscopy

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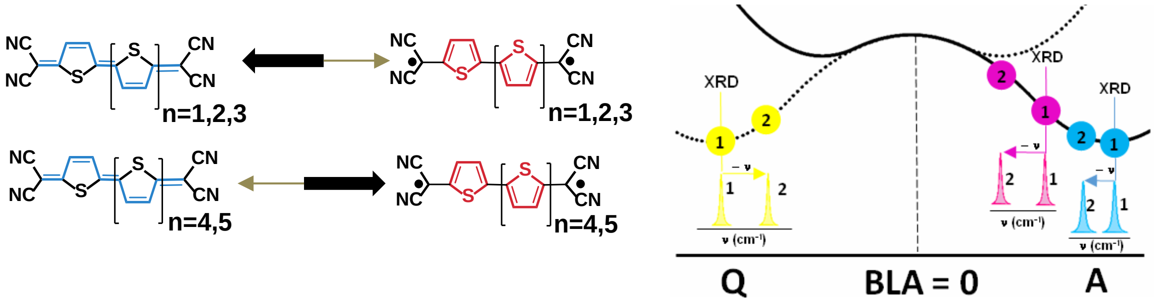
The vibrational Raman spectra of several series of aromatic and quinoidal compounds have been analyzed considering the down-shifts and up-shifts of the frequencies of the relevant Raman bands as a function of the number of repeating units.[1]



Scheme 1. Left: Quinoidal oligothiophenes and their conversion into aromatic diradicals. Right: Ground electronic state bond length alternation curve and Raman shifts.

Oligothiophenes (Scheme 1), oligophenylene-vinylenes, oligoperylenes (oligophenyls) and nanographene derivatives are studied in a common context.[2,3,4] These shifts are taken as spectroscopic fingerprints of the changes in π–conjugation and on the formation of diradical species. For a given family, aromatic and quinoidal oligomers have been studied together and according with their Raman frequency shifts located in the two-well BLA-energy curve of their ground electronic state (Scheme 1) as a function of the bond-length-alternation pattern (BLA). The connection among BLA, π–conjugation and Raman frequencies is taken here as the basis of our study. These Raman shifts/BLA changes have been related to important electronic properties of these one-dimension linear π–electron delocalized systems such as quinoidal (polyene) and aromatic characters as a result of the formation of diradical structures.

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BRIGHT AND STABLE NANOMATERIALS FOR IMAGING AND DIAGNOSTICS

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Luminescent nanomaterials are used in many applications, from advanced imaging techniques to biodiagnostics, etc. The ability to increase the brightness and photostability of these materials have direct impact on their performance, lowering the limit of detection in diagnostic applications and allowing their use in demanding laser scanning imaging techniques.

This communication focus on our use of different approaches to obtain materials with large brightness, based on polymers [1,2], silica nanoparticles [3-5] and hybrid nanostructures containing metal nanoparticles [6-8]. In polymers and in silica nanoparticles the increased brightness relies on the presence of multiple dyes on each chain/particle, while minimizing the interaction between the dyes to avoid emission quenching. On the other hand, in metal-containing hybrid nanostructures we want to use the plasmonic effect to increase the brightness of each dye.

Acknowledgements

This work was partially supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER), projects UID/NAN/50024/2013 and PTDC/CTM-POL/3698/2014.

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PHOTOCHROMIC SUPRAMOLECULAR HOST-GUEST SYSTEMS

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The development of systems able to exist in different states whose interconversion can be controlled by different stimuli (light, ions, electrons) may contribute to the appearance of molecular-level devices and materials with new functionalities. Over the last few years, we have worked in systems mainly based on *trans*-2-hydroxychalcones.[1] These photoisomerizable compounds originate in aqueous solution intricate pH-dependent chemical reaction networks involving several species. Among these species, flavylium cations are strongly coloured compounds that have been allowing to explore these chemical networks as pH–coupled photochromic systems, responding thus to pH and light.

As aromatic cations, flavylia are electron poor guests able to intercalate into neutral or negatively charged electron rich cavities such as those of molecular clips[2] and cucurbiturils.[3] This allows the use of supramolecular interactions to further control the conversion between different states of the system through functional host-guest complexes with potential applications in drug-delivery, molecular switches, molecular machines, supramolecular polymers, etc. Recent examples of these multistate systems exploited as photochromic,[4] pH-driven self-sorting,[5] and in particular, pH-gated photoresponsive pseudorotaxanes with ring translocation[6] will be shown.

On the other hand, the influence of supramolecular complexation with differently sized cucurbiturils on the photoinduced ring-closure reaction of symmetric dithienylethene derivatives bearing pyridinium moieties will also be shown.

This work was supported by LAQV-REQUIMTE which is financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265), and by project H2020-MSCA-RISE-2016 ID 734834 INFUSION (EU).

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FLUORESCENT DYES INTO 1D-ZEOLITIC MATERIALS FOR OPTICAL APPLICATIONS

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Materials with 1D-nanochannels with diameter size in the range of molecular dimensions are considered ideal host for supramolecular organization of photoactive guest molecules. The synergy of the confinement effect of organic dyes with good photophysical properties (strong absorption and fluorescence bands, lasing and NLO properties) hosted into rigid inorganic molecular sieves with good intrinsic physical properties (good mechanical, thermal, photo and chemical stabilities and optical transparency in the Vis-NIR radiation) ensures the achievement of new interesting optoelectronic and photonic devices. In this sense new generation of functional materials based on the anisotropic alignment of dyes into zeolitic matrices with one-dimensional channels of molecular dimensions have already been demonstrated.

Therefore, a good fitting between the pore size and molecular structure is relevant in order to avoid undesirable aggregates and to achieve the preferential orientation of the guest. In this sense, the crystallization inclusion method, where the guest dye is occluded in the porous host during the crystallization of the framework, should allow a very tight fit between the molecular and channel dimensions, which could not be accomplished by diffusional post-synthesis methodologies (due to diffusional restrictions). Thus, rational choice of the host structure with pores that perfectly matches the size of a desired organic dye is required.[1]

In this work, different chromophores have been encapsulated by crystallization inclusion method into the 1D-nanochannels of aluminophosphate crystals with different pore size. The final solid hybrid materials show interesting optical applications such as i) one-directional antenna systems[2] ii) fluorescence colour switches[3] iii) second harmonic generation materials[4] and iv) white light emitters (Figure 1)

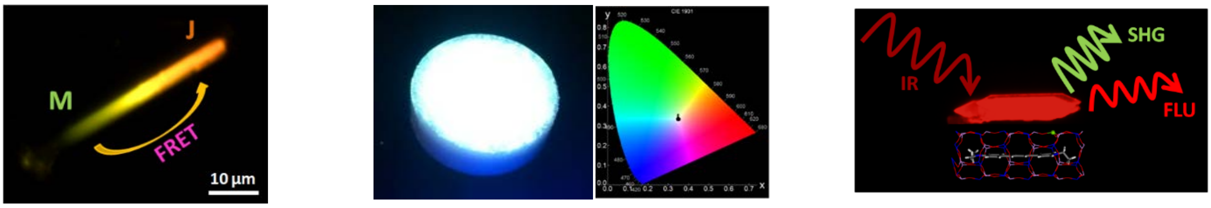

Figure 1. Examples of an antenna system (left); white light emitter material (middle) and SHG device (right)

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CHALCOGENIDE CHEMISTRY APPLIED IN THE SYNTHESIS OF NOBEL NANOMATERIALS: THE ROLE OF LIGHT AND WATER

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Since the first Faraday's report[1] on the synthesis of gold colloidal, considerable effort has been done to discover new synthetic routes which allow the design of nanomaterials with specific properties. Application of Heavy Chalcogenide Elements as Organo-chalcogen precursors (Se and Te) used as reducing/ stabilizers in the synthesis of multifunctional nanomaterials is an actual challenge, and a chemical hot topic for the future. Follow our research interests in multifunctional nanomaterials, we have reported recently a new methodology to produce long term preserved gold and platinum nanomaterials, either in solution, and in solid state.[2,3] The new synthetic protocols take advantage of the photochemical and oxidative properties of organic ditellurides (R_2Te_2), which so far has never been exploited in the synthesis of gold and platinum nanoparticles. The effect of oxygen, water and light will be discussed, as well as, a detailed mechanistic formation. Application of these materials in analytical environmental chemistry, proteomics and in the synthesis of anisotropic materials will be highlight.[4]

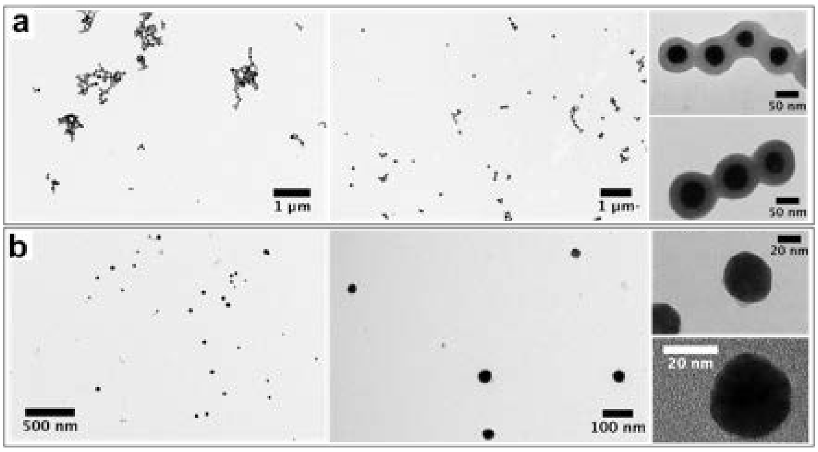

Figure 1. Low magnification TEM images of the Au-Te nanoparticles

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4. Patent: New Synthetic methodology for the synthesis of Metallic Nanoparticles using Chalcogen derivatives. Application form: No: BR 10 2015 018736 0. Javier Fernandez Lodeiro, Carlos Lodeiro, Alcindo A. Dos Santos.

MOLECULAR ENGINEERING OF TWO-PHOTON ABSORBING FOUR-COORDINATE ORGANOBORON FLUOROPHORES

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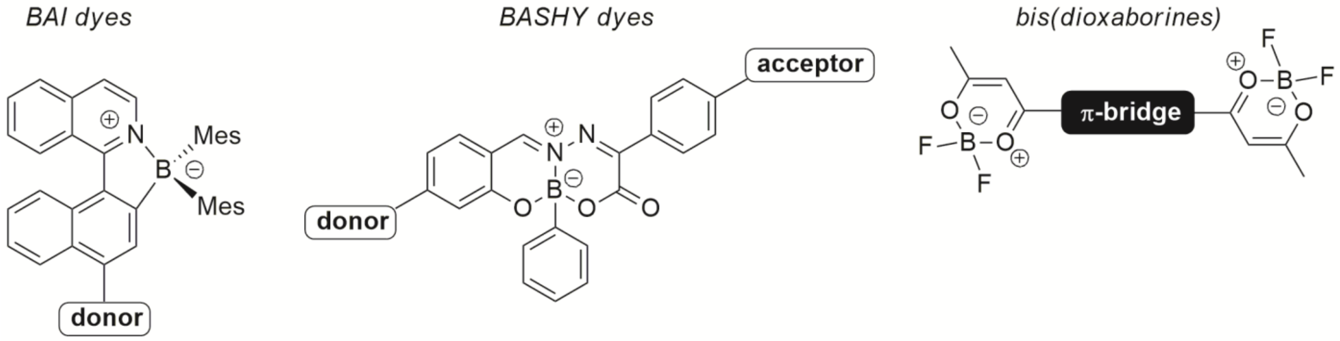
The design and photophysical optimization of chromophores that possess the ability to populate their emissive excited states by virtue of the absorption of two low-energy photons has attracted considerable interest during recent years.[1] Popular applications, where two-photon absorption processes are of advantage, are photolithography and bioimaging with confocal fluorescence microscopy. Two widely employed molecular design strategies, that are followed to arrive at efficient two-photon absorbers, are: (a) architectures that integrate electron donors and acceptors or (b) structures that count only either on acceptor or on donor moieties.

In our research program, related to the expansion of the pool of four-coordinate organoboron chromophores, we have made use of these design approaches to provide novel fluorophores that show high brightness combined with strong to exceptional two-photon absorption properties. These structures include N,C-chelates building on borylated arylisoquinolines (BAI dyes),[2-4] boronic acid derived salicylidenehydrazone complexes (BASHY dyes)[5,6] or bis(dioxaborines) with electronically variable π-bridges (see Figure below for general structures).[7] In this presentation I will give an overview of the photophysical rationales that are behind these structures and show some preliminary results of bioimaging applications.



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INVITED LECTURES

EXCEPTIONAL OPTICAL FEATURES OF LEAD HALIDE PEROVSKITES

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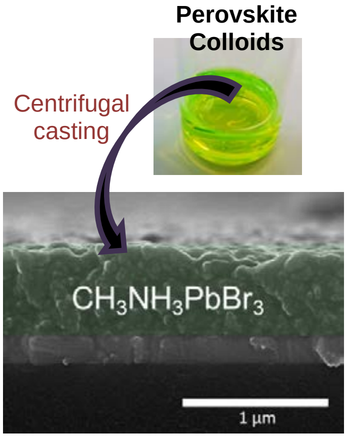
Hybrid organic-inorganic lead halide perovskite nanoparticles (NPs), such as $CH_3NH_3PbBr_3$ NPs, exhibit i) a strong and broad absorption spectrum; as a consequence, they are colorful solids and they form colorful colloids, ii) a narrow fluorescence band with a small Stokes shift, and iii) a relatively long-lifetime of up to microseconds; it was expected to be of a few nanoseconds for a direct gap semiconductor with a high absorption molar extinction coefficient. [1] The first synthesis of colloidal hybrid lead perovskites was reported in 2014, by using a medium/long alkyl ammonium bromide as the organic capping to confine the $CH_3NH_3PbBr_3$ perovskite at the nanoscale (ca. 6 nm) and allow its dispersibility in low-to-medium polar organic solvents. [2] CdSe colloids have been studied during more than two decades and share most of these features.

However, there are striking differences between these two kinds of NPs. The preparation of highly crystalline and emissive CdSe NPs requires high temperatures, whereas $CH_3NH_3PbBr_3$ NPs are prepared by using very mild reaction conditions. In spite of a good organic capping, CdSe NPs exhibit low emission quantum yield (usually smaller than 10%) and, therefore, they need to be electronically surface-passivated with several layers of a wider band gap inorganic material, such as ZnS, to lead to highly emissive NPs (up to 95%).[3] On the contrary, it has recently been demonstrated that i) $CH_3NH_3PbBr_3$ NPs without organic capping ("naked" NPs) can be prepared[4] and they show higher quantum yields than the ligand-capped CdSe NPs, and ii) $CH_3NH_3PbBr_3$ colloids can be prepared with a ca. 100% photoluminescence quantum yield and a low tendency to aggregate in solution by selecting the proper organic ligands; [5] these colloids self-assembled on a substrate efficiently, leading to NPs solid films of a considerable thickness while preserving a high quantum yield. The figure shows the cross-sectional SEM images of a $CH_3NH_3PbBr_3$ film (scale bar 1µm) prepared from the perovskite colloidal film of ca. 700 nm thickness) [6] The exceptional optical features of lead halide perovskites will be discussed.



Acknowledgements: We thank the Spanish Ministry of Economy and Competitiveness for funding (project CTQ2017-82711-P partially co-financed with FEDER funds, Maria de Maeztu: MDM-2015-0538.

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PHOTOACTIVE NANOCLUSTERS EMBEDDED IN SELF-ASSEMBLED FIBRILLAR NETWORKS

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Several self-assembled fibrillar networks (SAFINs) interfaced with inorganic nanostructures have been reported in the past (from gold, silver or magnetic nanoparticles to semiconductor quantum dots). Such SAFINs are formed by small molecular weight molecules showing a strong tendency to align in one direction, leading, eventually, to immobilization of the surrounding solvent, then affording macroscopic gels (hydrogels or organogels depending on the medium). A number of photonic applications of such hybrid organic-inorganic ensembles have been described.[1][2]

Hexanuclear molybdenum clusters have been reported to have interesting photophysical properties. For instance, they are highly luminescent (phosphorescence), with emission quantum yields close to unity in deoxygenated medium. Besides, they also show high capacity to generate singlet oxygen upon irradiation in aerated conditions, which opened the way for applications in photodynamic therapy.[3][4] However they have never been associated to any SAFIN.

Here we report the preparation of a series of SAFINs embedding one of those molybdenum nanoclusters (Figure 1) and their corresponding chemical and photophysical characterization.

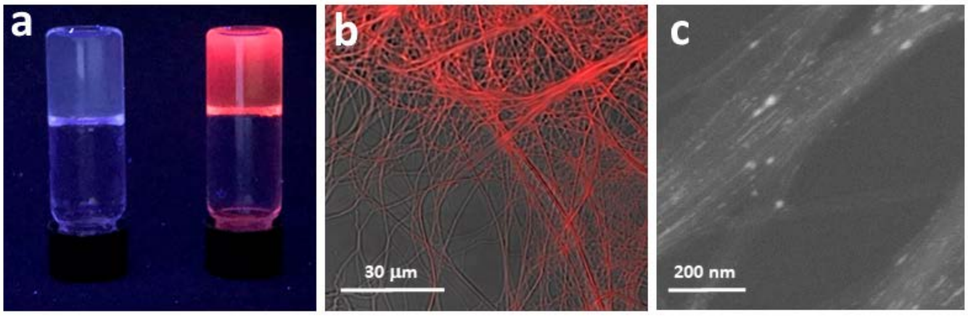

Figure 1. (a) Picture of an organogel material (left) and the same material embedding a hexanuclear molybdenum cluster (right), under UV illumination. (b) Confocal microscopy image of the fibers showing the red emission of the Mo cluster. (c) STEM image of the same fibers showing the Mo clusters as white dots.

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PIEZOPHOTONICS

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The deactivation of a previously excited molecule proceeds by the conjugation of two routes: radiative decay and non-radiative decay. Radiative decay through fluorescence or phosphorescence constitutes the motivation for most works within the photophysics and photochemistry field. On the contrary, the present work is stimulated by the heat generation capacity of the non-radiative decay route. Our aim is to explore the opportunities opened by high absorbing molecules and materials that fast release into heat the excess energy obtained by light excitation. Fast deposition of heat in a confined thermal expansive space gives rise to an acoustic pressure wave. Piezophotonics in this context refers to the capacity of a material to produce pressure impulses when irradiated by a pulsed laser light source.

We discuss the enhancement of non-radiative decays in organic molecules and the strategies to produce light-to-pressure transducer materials capable of generating high frequency ultrasound. Carbon based materials will be considered. Guided by the fundamental theoretical understanding of the thermoelastic processes involved and by the ability to develop adequate chromophores and substrates for light-to-pressure transduction, we were able to develop applications in three distinct fields:

i) Skin permeation: Pressure waves with 1 MPa amplitude and center frequencies of 100 MHz can be produced using designed piezophotonic materials and relatively mild ns laser pulses. Those light induced pressure gradients perturb the hardly packed nonliving corneocyte cells embedded in a mixture of lipids that constitute the stratum corneum outer layer of the skin structure, expanding the extracellular domains, and promoting dermal delivery. The process is reversibility that allows skin to recover its protective function.[1,2] Efficient intraepidermal delivery of large molecules employed in photodynamic therapy, hyaluronic acid and large proteins will be presented.[1,2]

ii) Intracellular delivery: Photo induced pressure waves produce temporary mechanical deformations of the cell membrane and facilitate the delivery of plasmid DNA into cells.[3] We show that the high stress gradients produced when ps laser pulses are absorbed by piezophotonic materials enable the transfection in 10 minutes of a plasmid DNA encoding Green Fluorescent Protein in COS-7 monkey fibroblast cells with an efficiency of 5% at 20 °C. Transfection using light and piezophotonic materials is scalable, affordable, enables nuclear localization, with dosage is controlled by the laser parameters and has the potential to deliver almost any cargo molecule to any cell type with minimal cell perturbation.

iii) Imaging: Photoacoustic microscopy and imaging is being applied to cells, small animal studies and, more recently, in human diagnostics.[4] A photoacoustic contrast agent is characterized by a fast and close to unit efficiency of transduction of light into heat. Should have very low fluorescence quantum yield and should not be able to induce reactive oxygen species. Using a new exogenous contrast agent with high absorption in the near infra-red we observed light induced pressure waves originating from inside viable cells. The molecule showed no toxicity. Taking advantage of the high light-to-pressure transduction observed within cells we were able to perform cellular uptake assays.

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GOLD(I) COMPLEXES SELF-ASSEMBLY, LUMINESCENCE AND APPLICATIONS

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Metallogels are a subject of study in the last few years.[1] The reason for the growth of interest stems from the availability and the diversity of metal-ligand coordination that could readily induce or control the self-assembly process of the gel formation and thereby influence the gel properties, as a difference with what occurs in organic gels. Organometallic Au(I) complexes present the additional advantage to use both classical supramolecular interactions (e.g. π-π stacking or hydrogen bonding) together with the establishment of Au(I)···Au(I) bonds (aurophilic interactions), which are particularly strong. Furthermore, these complexes exhibit interesting emissive properties that usually are modulated by the presence of the aurophilic interactions, display sup-picosecond intersystem crossing rate constants[2] and can display thermally assisted delayed fluorescence (TADF) with short luminescence decay times and a high PL quantum efficiency[3], important properties for OLED emitters.

We have reported on the formation of luminescent Au(I) hydrogels based on water soluble organometallic alkynyl complexes where aurophilic intermolecular interactions are involved on the gelation process.[4-8] Slight modifications on the chemical structure can induce significant changes on the supramolecular assemblies leading to hydrogels, rods or vesicles.

Analysis of the thermodynamic and photophysical parameters that modulate and are modulated, respectively, by Au(I) and Au(I)...Au(I) interactions has been performed and the results are supported by theoretical data.

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Luminescent Zr-Based MOFs: From Fundamental to LED application

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The excess of global energy demand has urged the scientific community to develop new efficient smart-materials and devices capable to reduce the energy consumption. Among all the possibilities, Metal-Organic Frameworks (MOFs), a class of hybrid organic-inorganic crystalline porous compounds, have emerged as excellent materials for a wide range of energy-related applications.[1] Their excellent physicochemical properties such as relatively easy chemical synthesis, large specific surface area, and cavities accessible to different guests, convert MOF materials in an ideal candidate for energy storage and conversion.[1] The use of luminescent MOFs for lighting applications has also raised great attention due to their great versatility (the emission can be originated by the linkers, the metal-clusters or a combination of both), synthetic flexibility (exchange of linkers and metal clusters) and the possibility to encapsulate different fluorophores.[2-4] However the use of luminescent MOFs in the fabrication of low-consumption energy devices as light emitting diodes (LEDs) remains almost unexplored. There are just few examples in the literature concerning to the use of MOFs for LED applications, and most of them consist on covering a UV-blue LED with the luminescent MOF material.[5]

Herein, we present the use of a Zr-NDC MOF (NDC= 2,6-naphtalene dicarboxylate) and different guest@Zr-NDC (guests= Coumarin 153 (C153) and DCM) composite materials as the electroactive layers of new LEDs (Figure 1A).[6-7] To this end, it is paramount to unveil the photoluminescent properties of these materials, and we have reached this aim by using different steady-state and time-resolved techniques. From these experiments, we have established that the Zr-NDC emission is due to monomers (3-4 ns) and excimers (13-14 ns) of the NDC linkers (Figure 1B).[2] When C153 and DCM dyes are encapsulated into Zr-NDC MOF, an energy transfer from Zr-NDC MOF to each dye is observed upon irradiation. [3] Moreover, we have also demonstrated that both, the excimer formation in Zr-NDC and the energy transfer from Zr-NDC to encapsulated guests, are still occurring when the materials are dispersed into polymeric matrixes, which is essential for further incorporate these materials into the LED devices.[4] The results clearly show how time-resolved techniques are essential to unravel the photoproperties of MOFs and how they have the potential to be used as new tunable electroluminescent materials for LED applications.

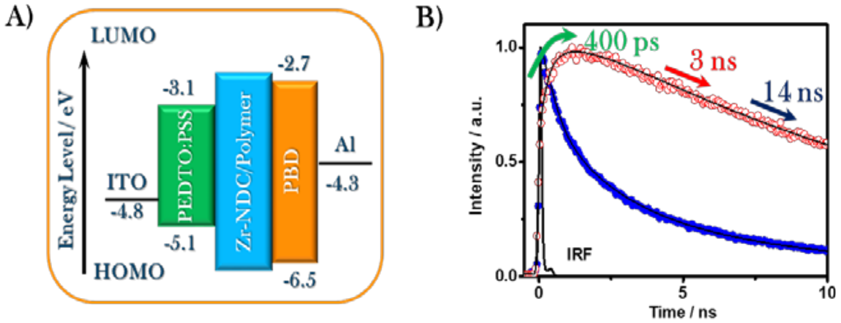

Figure 1. A) Schematic representation of the MOF-LED device architecture. **B)** Time-resolved emission decays of Zr-NDC. The excitation wavelength was 371 nm and the observations were 405 nm (blue line) and 500 nm (red line). The indicated times correspond to NDC excimer photoformation (400 ps) and NDC monomers (3 ns) and excimers (14 ns) emission lifetimes.

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SHINING NEW LIGHT ON ANCIENT FORMULATIONS: PREPARATION AND PHOTO-PROPERTIES OF CARBON NITRIDES

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Carbon nitride (C_3N_4) owning high chemical stability and being easy to prepare [1] shows remarkable properties as photocatalyst in spite of its wide bandgap of 2.7 eV. The base of this material has its origins in the synthetic work of Johann Jakobe Berzelius and Justus von Liebig, in 1834, who isolated a polymeric carbon nitride material called melon. This material presented a lamellar structure, due to staking of several graphite-like sheets possessing a π-conjugated structure, owing to the sp^2-hybridization of the carbon and nitrogen atoms, which resulted in an optical semiconductor material with photocatalytic properties.

Yet, the photocatalytic performance of C_3N_4 is normally affected by the fast electron-hole recombination. A promising strategy for increasing C_3N_4 efficiency is by coupling with carbon materials such as carbon nanotubes and graphene derivatives, the hybrid materials normally showing enhanced electronic properties [2].

In this contribution some applications of these materials will be highlighted, namely the selective photocatalytic oxidation of benzyl alcohol to benzaldehyde by using metal-loaded C_3N_4 photocatalysts [3]. The use of novel hybrids of carbon nitrides sensitized with free-base porphyrins for efficient visible light photocatalytic hydrogen production will be also addressed [4]. Some environmental applications such as using carbon nitride nanosheets as highly efficient photocatalysts for phenol degradation under high-power visible LED irradiation will be also discussed [5]. Finally, some operational aspects and concepts on the preparation, characterization and photocatalysis under visible LED irradiation will be discussed in the case of nanocomposites made of SnO_2 and C_3N_4 [6].

Finally, comments and trends in the nomenclature and desired properties of these materials will be discussed.

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Perylenediimides as building blocks for functional nanomaterials

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Perylenediimides (PDIs, Figure 1) show interesting properties, such as near-unity fluorescence quantum yield, excitation in the visible region, strong and reversible electron-accepting character, and high electron mobility. PDIs start to be used as industrial pigments for tissues and paints (1910s-1980s), but recently they have been extensively studied as organic field-effect transistors, as fluorescent solar collectors, in organic photovoltaics, or as bioimaging agents. The synthesis of PDIs derivatives, starting from the commercially available perylene-3,4,9,10-tetracarboxylic acid dianhydride, allows the selective introduction of substituents in the imide group or in the bay region (Figure 1).

This communication will shows how bay substituents induce different torsion angles to the perylene core [1] or tune the photophysical properties (visible to NIR fluorescent emission)[2] and how PDIs can be introduced in different nanostructures through specific imide substituents.[3] Additionally, our recent efforts to developed new water soluble PDIs for imaging and 3D optical nanoscopy will be reported.

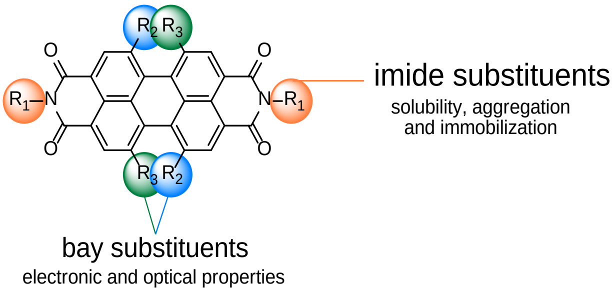

Figure 1: PDIs general structure and influence of the different substituents position.

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MAGNETOLIPOSOMES AS NANOCARRIERS FOR FLUORESCENT POTENTIAL ANTITUMOR DRUGS

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Magneto-sensitive liposomes can be obtained by encapsulation of magnetic nanoparticles into liposomes or by the coverage of magnetic nanoparticles with a lipid bilayer. The so-called magnetoliposomes make possible to explore the synergistic effect between chemotherapy and magnetic hyperthermia. Recently, both aqueous magnetoliposomes (AMLs, containing magnetic nanoparticles entrapped in liposomes) and solid magnetoliposomes (SMLs, where clusters of nanoparticles are covered by a lipid bilayer) containing several different nanoparticles (magnetite, nickel ferrite, manganese ferrite or magnesium ferrite) have been developed,[1-4] exhibiting a superparamagnetic behavior and diameters below 150 nm (figure 1A).

These nanosystems were successfully tested as carriers for fluorescent potential antitumor drugs.[2-4] Fluorescence-based methodologies (FRET, emission quenching and fluorescence anisotropy) have been employed as valuable tools for this investigation. Drug-loaded magnetoliposomes have shown the ability to interact by fusion with GUVs (giant unilamellar vesicles, used as models of biomembranes)[1-3] (figure 1B) and to release the antitumor drugs in *in vitro* assays using human tumor cell lines,[4] being promising for the development of a dual therapy of cancer (combining chemotherapy and magnetic hyperthermia).

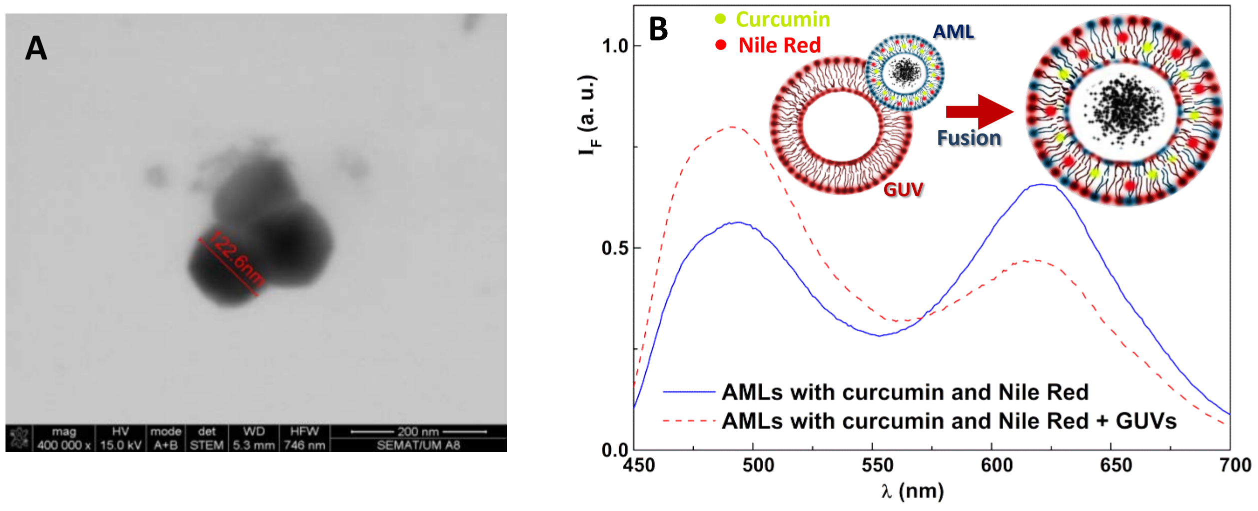

Figure 1. A: STEM image of solid magnetoliposomes (SMLs) based on Fe_3O_4 nanoparticles. **B:** Fluorescence spectra of aqueous magnetoliposomes (AMLs) containing both curcumin (as energy donor) and Nile Red (as energy acceptor), exciting only curcumin, before and after interaction with GUVs.

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PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF CYCLOMETALATED PLATINUM(II) AND PLATINUM(IV) COMPLEXES

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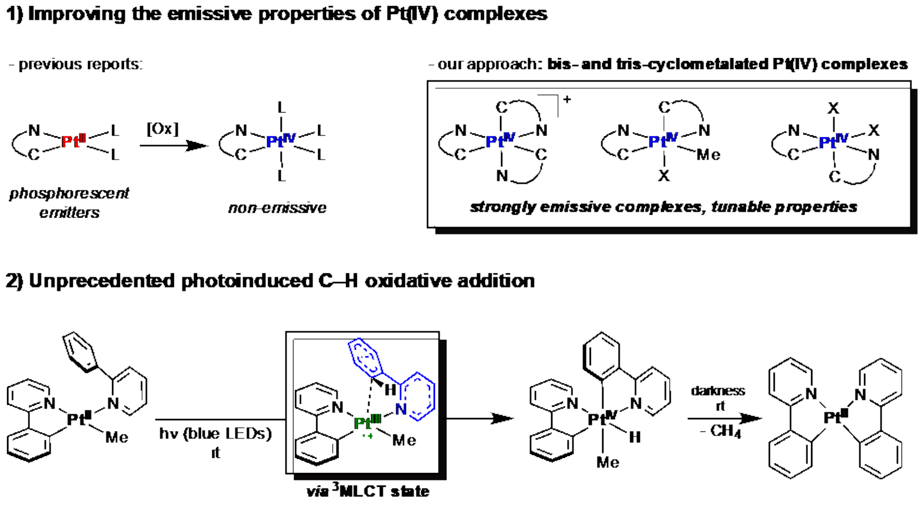
Here are described some of the results obtained after four years of research in the photophysics and photochemistry of cyclometalated Pt(II/IV) complexes. Two major aims can be observed:

(1) *Quest for highly efficient Pt(IV)-based emitters*. In spite of the large amount of references devoted to the study of the photophysical properties of other metal complexes with d^6 electronic configuration (*i.e.* Ru^{2+}, Ir^{3+}),[1] Pt(IV) seemed to be overlooked in this research field owing, in part, to the extensive attention attracted by Pt(II) systems. In fact, processes involving the oxidation of Pt(II) to Pt(IV) are often considered disadvantageous for luminescence purposes, as typically result in non-emissive compounds.[2] This is caused by the high electrophilicity of Pt(IV), which results in lower-energy d and d*(Pt) orbitals in comparison with other d^6 metal and Pt(II) complexes. In order to overcome these drawbacks, we designed tris- and bis-cyclometalated complexes as suitable candidates to achieve efficient emissions in Pt(IV) systems, reaching phosphorescence quantum yields up to 81%, the highest ever reported for Pt(IV) emitters.

(2) *Study of the photochemical C–H oxidative addition in Pt(II) complexes*. During the course of our research, we discovered that visible-light irradiation produced the photochemical cyclometalation of coordinated phenylpiridine in a Pt(II) complex at room temperature. Mechanistic studies revealed an unprecedented photoinduced C–H activation mechanism, initiated by the population of a ^{3}MLCT state that involves a charge transfer to the coordinated aromatic compound, leading to a Pt(IV) methyl hydride intermediate, *the first detected in any cyclometalation reaction in Pt(II)*. Despite being a formal oxidative addition, this photochemical C–H activation is fundamentally different from the traditional ground-state pathway and *has no precedents in metal- mediated C–H activations*.



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NIR-RESPONSIVE NANOHYBRIDS FOR EFFICIENT ENERGY TRANSFER

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$NaYF_4$ nanoparticles (UCNPs) co-doped with lanthanides cations (e.g., Er^{3+}, Yb^{3+}, Tm^{3+}) are fluorescent nanoparticles (NPs) able to emit in the visible upon excitation at the near-infrared (NIR) due to their intra-configurational 4f electron transitions. In addition, UCNPs exhibit excellent chemical and optical features, such as high (photo)stability, good biocompatibility, narrow bandwidth, long luminescence times, no photoblinking and no photobleaching. [1] Thus, UCNPs are widely used as energy donors in resonance energy transfer (RET) processes for many applications, e.g., photocatalysis, biosensing or photodynamic therapy (PDT). [2] There are three main requirements for efficient RET from UCNPs to an energy acceptor (e.g., organic dye, luminescent NP) after excitation with NIR light: i) strong spectral overlap between the UCNP emission and the acceptor absorption; ii) highly emissive UCNPs; and iii) the energy acceptor must locate very close to the UCNP surface in order to maximize the RET efficiency. [2]

The spectral overlap can be achieved by carefully choosing the energy acceptor. The control of the reaction parameters as well as the composition of the NPs allow us to optimize the UCNP emission. We have demonstrated the influence of the reactants addition temperature and the reaction temperature on the size and shape of the UCNPs. [3]

Finally, the donor-acceptor distance can be manipulated through the surface chemistry, which it is crucial in the nanohybrid design. [1] We have developed two different methods to modify the UCNP periphery to obtain efficient RET. One strategy is based on the direct interaction of the anchoring group of the functional ligand: the carboxylate group of a BODIPY derivative (BDP, a singlet oxygen photosensitizer (PS)) anchors to the NP surface leading to UCNP@BDP nanohybrids. [4] The direct anchoring facilitates a high loading of the PS and avoids its leaching from the nanohybrid. In vitro studies using SH-SY5Y human neuroblastoma-derived cells show the potential application of UCNP@BDP nanohybrids in NIR-induced PDT. [5]

The second method uses a water-soluble, symmetrical macrocycle, in particular cucurbit[7]uril (CB[7]), which possesses two carbonyl portals.[6] The spontaneous adsorption of CB[7] on the surface of naked UCNPs leads to UCNP@CB[7]. These nanohybrids are able to form exclusion complexes with organic dyes (such as methylene blue and pyronine Y), as well as with luminescent NPs (such as perovskite NPs (PK)) via the CB[7] carbonyl free portal. [7] This strategy makes it possible to locate a high concentration of the energy acceptor closely and firmly to the UCNP surface and, as a consequence, efficient RET from the UCNP to the energy acceptor is observed after NIR-excitation. These studies have been performed at the Molecular Science Institute of the University of Valencia (Spain).

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF FUSED-PHTHALOCYANINE SYSTEMS

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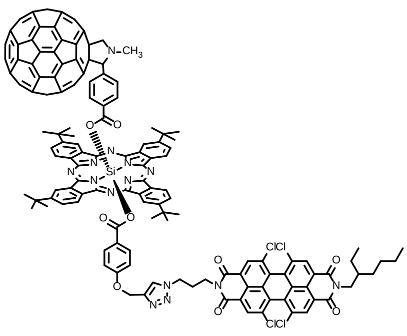
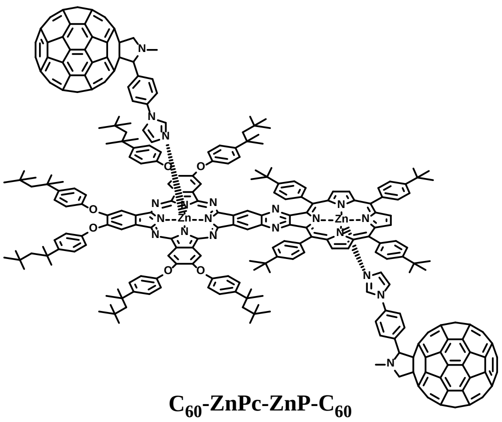
In the past last decades, a formidable effort has been devoted to the synthesis of donor–acceptor artificial scaffolds capable of mimicking the light-harvesting complexes of natural photosynthesis in order to build low-cost photovoltaic devices.[1]

We describe here the synthesis and photoinduced sequential energy transfer followed by electron transfer in new covalently and supramolecularly linked multichromophoric ensembles. Different arrays have been prepared combining donor and acceptor moieties, such as phthalocyanine (Pc), perylenediimide (PDI), diketopyrrolopyrrole (DPP), porphyrin (P) and C_{60}, as the represented in the Figure: C_{60}-SiPc-PDI[2] and C_{60}-ZnPc-ZnP-C_{60} [3] . Some of these systems have also been incorporated as active components in solar cells.



C_{60}-SiPc-PDI



C_{60}-ZnPc-ZnP-C_{60}

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ORAL COMMUNICATIONS

Naphthyridine-based Gold(I) complexes: new tools for nucleotide sensing using Aggregation Induced Emission

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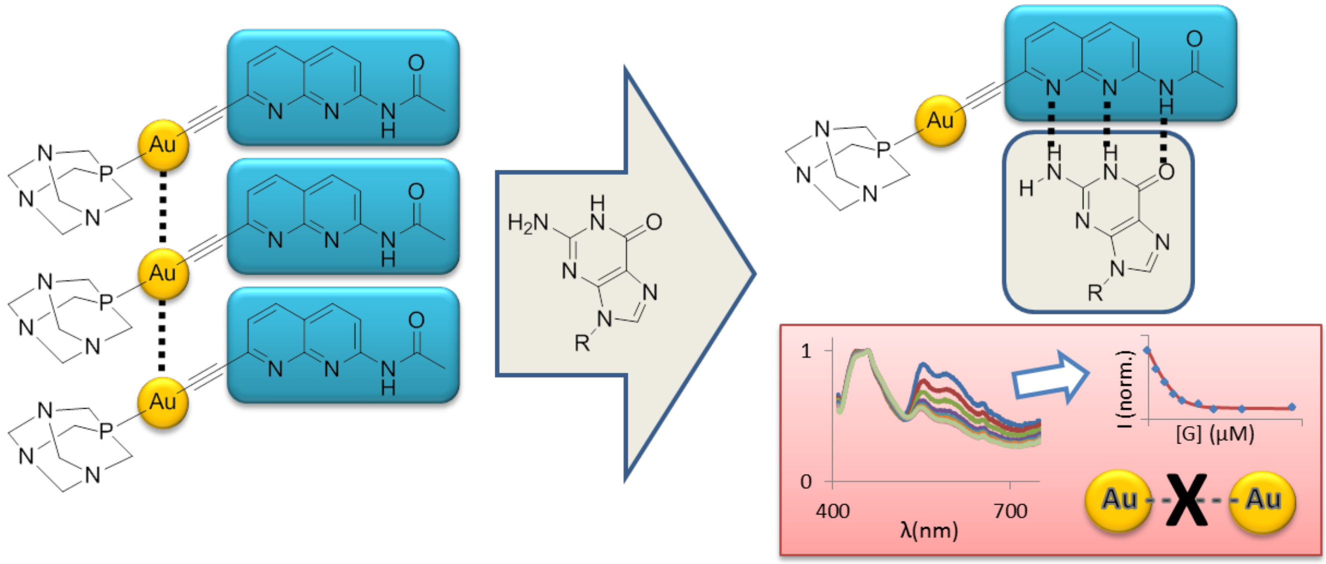
Aggregation Induced Emission (AIE) is currently a hot topic in the scientific community, as it can be used for developing a plethora of new luminescent tools and materials with specific emissive characteristics.[1] Our recent work with Gold(I)-alkynyl complexes has led us to discover their AIE properties due to the establishment of aurophilic interactions [2], which can be modulated either by changing their concentration and solvent [3], or by applying external stimuli.[4] Following up on this recent research, we designed two new Naphthyridine-Au(I) complexes, which exhibit AIE in the visible region of the spectrum. Sensing of Guanine nucleotides is achieved via disruption of the aggregates/aurophilic bonds. These results highlight the unique potential of these complexes as sensors for specific nucleotides larger biomolecules (RNA/DNA) through base-pairing interactions in aqueous media.



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Hybrid Gold Nanoclusters-Polymer Nanoparticles as Fluorescent Probes

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Gold Nanoclusters (AuNCs) are a new type of gold nanostructures with a few gold atoms and dimensions below 2 nm. They have been increasingly studied due to their unique optical properties: size dependent luminescence and very high photostability[1]. Other properties, such as low toxicity and biocompatibility, also contribute to their potential wide range of applications across different fields, from medicine and biology to physics and chemistry, including catalysis, sensing, imaging and theranostics[2].

Our main interest is in the application of AuNCs as labels for advanced optical imaging. The goal is the development of novel AuNCs contained in nanomaterials that may overcome the poor stability of single AuNCs. Our approach is the incorporation of AuNCs in polymer nanoparticles through photoinduced miniemulsion polymerization[3], allowing the AuNCs to maintain their optical properties, in particular for wavelengths in the near infrared (NIR), with higher tissue penetration. We prepared and characterized hybrid polymer-AuNCs nanoparticles with diameters around 50 nm (Figure 1), high colloidal stability and good optical properties, emitting in the NIR region.

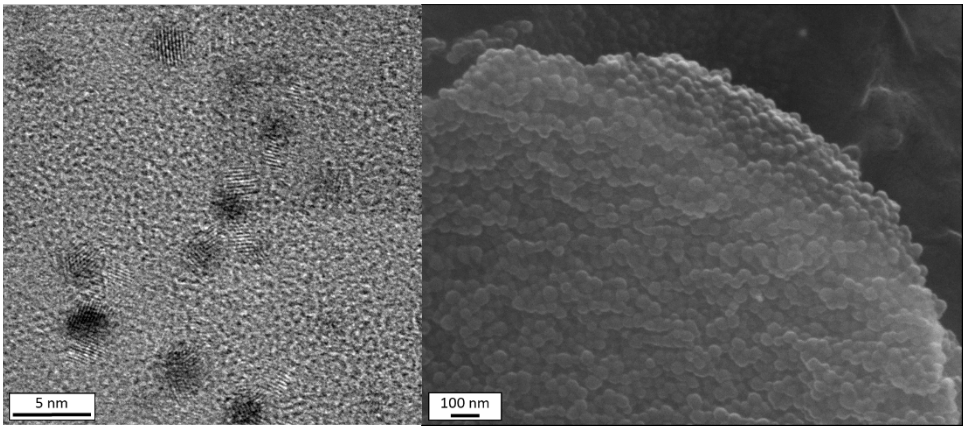

Figure 1. HR-TEM of AuNCs (left) and SEM of polymer nanoparticles containing AuNCs (right).

Acknowledgements

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Anisotropic Gold Nanoantennas for Enhancing Fluorescence Detection: from Single to Dimer Nanoparticles

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Good fluorescent dyes have emission quantum-yields close to one, but their absorption cross sections are typically smaller than the molecule's physical dimensions, which limits the dye's excitation rate. Metal nanoparticles can act as optical antennas and provide a way to overcome this limitation. The dye's excitation and decay rates can be enhanced by orders of magnitude in the vicinity of a metal nanoparticle [1]. In this contribution, we will present our results on fluorescence enhancement of red-emitting dyes induced by anisotropic gold nanoantennas. The enhancement effect of single gold nanorods on the emission of ATTO-647N dye was evaluated by single-molecule fluorescence microscopy. The stochastic interactions of the dye diffusing in solution with surface-immobilized gold nanorods gives rise to strong bursts of enhanced fluorescence. From theoretical simulations, we have predicted that the maximum enhancement occurs at dye-to-particle distances around 3 to 4 nm away from the nanorod's tips. For this reason, in this study we have used a thiolated ds-DNA linker with a length of 10-bp in order to match the optimal distance. The maximum enhancement events measured in our single-molecule experiments correspond to an emission increase by two orders of magnitude, which agrees with the simulations. These results highlight the importance of site-selective approaches for hot-spot functionalization in order to maximize plasmonic effects [2]. Another example is that of gold nanodimers prepared by DNA-directed self-assembly. The nanodimer antennas were assembled from spherical gold particles using doubly-thiolated ds-DNA linkers to achieve narrow interparticle gaps. Gold nanodimers are powerful antennas for emission enhancement because of the large plasmon fields that can be reached in the gap hot-spots. Indeed, it was possible to measure top emission enhancements of three orders of magnitude for ATTO-655 dye [3]. The gold nanodimers were further evaluated for emission enhancement of porphyrins, which are known to be poor emitters. As expected, the antenna effect is relatively more pronounced and top enhancements of million-fold were observed in this case. The application of gold nanoantennas for nucleic acid detection by fluorescence signaling will be discussed, in view of the advantages and limitations toward increasing detection sensitivity in biosensor devices.

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SENSING 1,3-DICARBONYL TOXINS WITH LUMINESCENT RUTHENIUM(II)-POLYPYRIDYL COMPLEXES

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1,3-Dicarbonyl compounds are among the most important intermediates in organic syntheses. They are also employed as fuel additives, biologically active species (e.g. fluoroquinolone antibiotics or curcumin), and substrates for preparation of hydrophobic polymers.[1] However, some natural dicarbonyls may have adverse effects on human health. This is the case of **tenuazonic acid** (TeA), a mycotoxin produced by *Alternaria fungi* that contaminate a large fraction of the world's food.[2] Therefore it makes especially interesting the development of sensitive, selective and straightforward analytical methods for its rapid detection and quantification in situ, without transporting the sample to the laboratory where expensive techniques such as LC-MS/MS are behind the current methods for toxin identification and determination.

When aiming to develop new sensing platforms, **luminescent** chemosensors are one of the best choices because of their high sensitivity, good selectivity, ease of miniaturization and field deployment. In this context, we have devoted significant efforts to the molecular engineering, preparation and photochemical characterization of luminescent **polypyridyl Ru(II) complexes**. These dyes show remarkable properties such as long (red) emission lifetimes (up to 6 μs, above 600 nm), with large Stokes shift (> 150 nm) and high (photo)chemical stability, together with the flexibility of finely tuning their photochemical properties and polymer-supporting method, by a judicious selection of their coordination sphere.[3] For *signaling* the presence of the target analyte, a **specific ligand** must be introduced in the complex, in such a way that the interaction with the target analyte induces a change on its luminescence. It is well known that 1,3-dicarbonyl compounds are relatively easy to deprotonate (e.g. the pK_a of TeA is 3.5), yielding an enolate anion stabilized by resonance. Taking into account the chemical properties and structure of the latter, we propose the use of **2,2'-biimidazole** (bim) ligand as a suitable *receptor*. When coordinated to Ru(II), this ligand can provide strong **hydrogen bonds** to the target molecule in a proper geometrical arrangement (Fig. 1), but not so much for other organic anions such as carboxylates, phosphates or sulfates, which predominantly bind to ureas. The photochemical properties of several *heteroleptic* Ru(II)-bim complexes, as well as their luminescent response towards TeA^- and other bidentate organic oxoanions such as acetate, will be discussed in this communication.

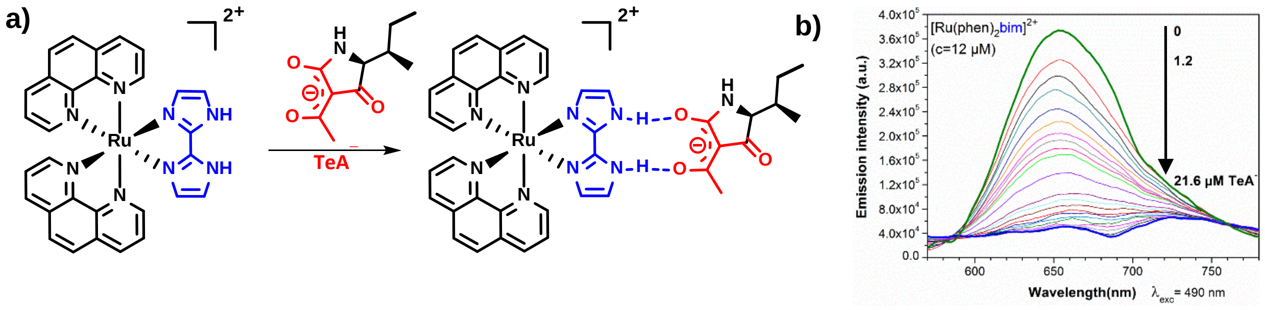

Figure 1. a) Example of the interaction between the Ru(II)-biimidazole complex $[Ru(phen)_2bim]^{2+}$ and the tenuazonate anion; b) Changes in the emission spectra of a Ru(II) complex in DMSO solution upon addition of TeA.

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Eu^{3+}-COMPLEX-BASED HYBRID MATERIALS FOR LUMINESCENT SOLAR CONCENTRATORS

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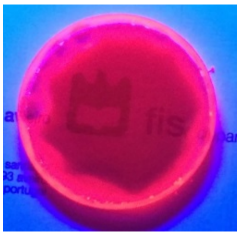
To make the solar cells cost-effective, we need to find materials or methods capable of exploiting sunlight with the highest possible efficiency. One promising strategy for achieving higher solar energy conversion efficiency is the use of luminescent solar concentrators (LSCs), which concentrate the solar energy by total internal reflection and guide it to the solar cells placed at the edge of the waveguide and thereby provide potential low cost energy production.[1] Down-shifting processes are ideal to improve the spectral responses of c-Si solar cells using LSCs. The unique photophysical characteristics such as high quantum yields, sharp emission bands, long luminescent decay times and large Stokes shifts make lanthanide-based complexes an excellent class of emitting materials for LSCs.[2] The poor photostabilities and mechanical processabilities of the lanthanide complexes often limited their practical applications in various optoelectronic applications. The thermal and photo stabilities of these complexes can be improved by embedding them into appropriate host matrices.[3]

We synthesized a series of luminescent Eu^{3+}-complexes, **1**-**3**, based on 2-thenoyltrifluoroacetone (**tta**) and 2,2′-dipyridyl N,N′-dioxide (**bpyO2**) ligands. The developed complexes have been characterized well with special emphasis on their luminescent properties. Single crystal structures of the developed complexes are determined and the structure-property relationship in these complexes will be described. Complex **3**, $\mathrm{Eu}(\mathbf{tta})_3(\mathbf{bpyO2})$ exhibited a broad excitation spectrum in the 250-450 nm region, and sharp emission peaks of Eu^{3+} ion. Compared to the corresponding solvated complexes, $\mathrm{Eu}(\mathbf{bpyO2})(\mathrm{H_2O})_4(\mathrm{Cl})_3$ (**1**) and $\mathrm{Eu}(\mathbf{tta})_3(\mathrm{H_2O})_2$ (**2**), complex **3**, exhibited attractive luminescence quantum yield (49%), and excited lifetime (0.454 ms) when excited at 400 nm.

To improve the photostability and mechanical processability (which are imperative for LSC applications) of complex **3**, it was embedded into a tri-ureasil-based organic-inorganic host material. The developed highly luminescent, transparent monolith (**4**) and thin film (**5**) retained the optical properties of the parent Eu^{3+}-complex. The hybrid materials also exhibited better photostabilities, compared to the precursor complex. Interestingly, the excited state lifetimes of the hybrid materials (0.602 ms for **4** and 0.589 for **5**) are found to be longer than that of the parent complex.

Under ambient light



Under UV-irradiation

The broad excitation spectra, of the parent complex (250-450 nm) and the developed hybrid materials (250-400 nm), which extended to the visible blue region, are significant, as the integral overlap with the solar spectrum is crucial for LSC application. So the developed organic-inorganic hybrid material may prove to be a good candidate to improve the efficiency of the Si-solar cells *via* luminescent down-shifting and further developments towards the LSC applications of the designed materials are progressing in our laboratory.

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ON THE ORIGIN OF THE EMISSION OF CARBON NANODOTS: MOLECULE-LIKE FLUOROPHORES VS NANOGRAPHENE-LIKE CLUSTERS

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Molecular materials with efficient nonlinear absorption have found application in optical imaging and sensing in biological media, microfabrication, data storage, photodynamic therapy and power limiting. Recent progress in nanoscience has enabled new kinds of nanostructured materials with improve nonlinear response that can have a real impact in society, among them lanthanide nanoparticle, metal nanoclusters and carbon dots.[1] Due to their optical properties, water solubility and ease of functionalization carbon dots (C-dots) became especially attractive as a platform for biomedical applications (imaging, sensing, drug-delivery).[2] Nevertheless, the largely ignored origin of their emission has precluded an insightful approach to their practical applications, which remains mostly driven by empirical evidence and curiosity.

In this presentation, emphasis will be laid upon our recent study on the nonlinear emission spectroscopy of nitrogen doped carbon dots (Figure 1).[3] We found that both linear and nonlinear emission can be understood based on the existence of isolated sp^2 clusters involved in $\pi-\pi$ stacking interactions with clusters in adjacent layers, with the biphotonic interaction being selective towards sp^2 clusters bearing electron donor and acceptor groups on the edge. Our comprehensive study provides an extra piece of the puzzle of the origin of photoluminescence emission in carbon dots.

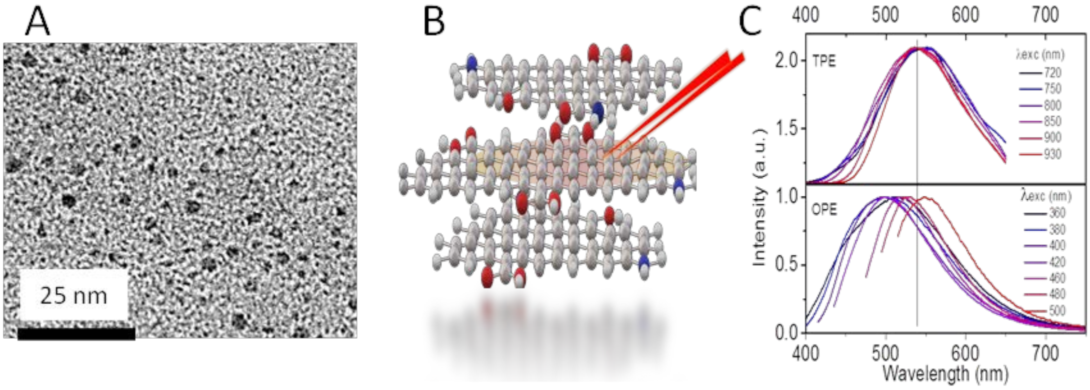

Figure 1. Carbon dots structure and emission spectroscopy: A, TEM image, B, representation of the selectivity of two-photon absorption in C-dots , two-photon and one-photon induced emission.

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“The membrane potassium channel KcsA - Exact analytical solutions for advanced homo-FRET to retrieve structural information”

M. L. Renart, A. Coutinho, J. A. Poveda, M. Giudici, A. Fedorov, M. Berberan-Santos, J. Gonzalez-Ros, M. Prieto

Donor decay ensemble average in FRET studies of biological systems usually only allow qualitative information about topology and structure. However, in systems of high symmetry, exact analytical solutions containing information about specific distances can be obtained, and used to fit high quality time-resolved data (usually within a global analysis methodology).

In this study, the tetrameric potassium channel KscA was engineered in order to have only a single tryptophan per monomer. An exact solution for homo-FRET within a square geometry was derived and fitted to anisotropy decays. The recovered distances will be compared with the ones from diffraction data, in both closed and open states, and for different ions. The advantage of this methodology over X-ray diffraction will be discussed.

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PHOTOCHEMISTRY OF ARYL NITRENES: DOORWAY TO ELUSIVE INTERMEDIATES AND TUNNELING REACTIONS

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We have recently experimentally observed a first tunneling reaction in the nitrene chemistry. [1] Triplet formyl-phenylnitrene ^{3}**2** was generated by UV irradiation in cryogenic matrices from formyl-phenylazide **1** and was characterized by IR, UV-vis, and EPR spectroscopies. The protium formyl-phenylnitrene ^{3}**2** (R = H) was found to spontaneously rearrange to singlet imino-ketene **3** (Figure 1), on the time scale of hours. The D-substituted triplet ^{3}**2** (R = D), under similar conditions, was found to be stable against spontaneous decay. [1] The distinctive behavior of the two isotopologues indicates that decay of the protium formyl-phenylnitrene ^{3}**2** (R=H) occurs via H-atom tunneling.

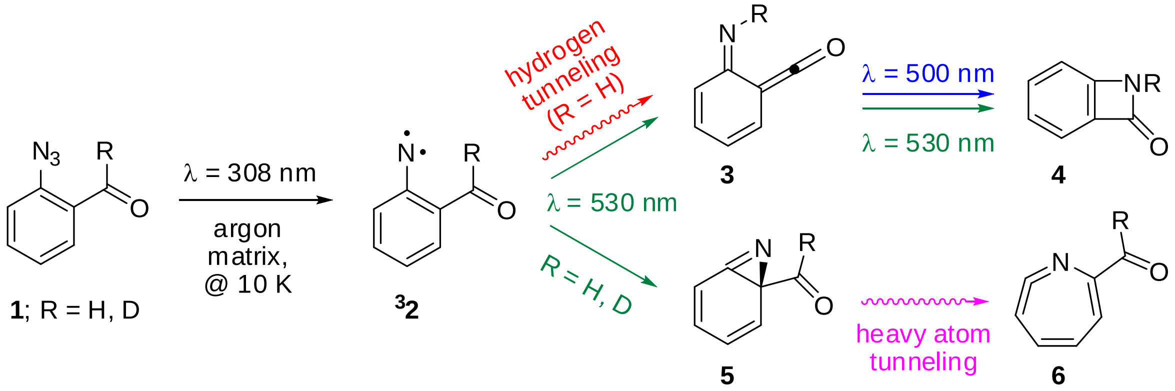

Figure 1. Reactions experimentally observed on the potential energy surface of the aryl nitrene ^{3}**2**.

Irradiation of nitrene ^{3}**2** (R = H, D) with visible (λ = 530 nm) light results in its phototransformation into imino-ketene **3**, as well as into elusive benzazirine **5**. [2] Imino-ketene **3** photorearranges (λ = 530 nm or 500 nm) into benzoazetinone **4** (Figure 1). Interestingly, we found that benzazirine **5** spontaneously rearranges, on the time scale of days, into cyclic ketenimine **6** (Figure 1), at 10 K and in dark, despite an estimated activation barrier of 7.5 kcal mol^{-1}. The identification of the reactants and the products, as well as their evolution, was carried out experimentally by IR spectroscopy and by comparison with simulated IR spectra. The rate constants without and with tunneling (using canonical variational transition state theory, and small curvature tunneling, respectively) were computed and confirmed that the observed spontaneous transformation of **5** into **6** can only occur by heavy atom tunneling. [2]

Acknowledgements

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DETERMINING A TOPOLOGICAL MODEL FOR TAU BOUND TO TUBULIN HETERODIMERS BY SMFRET: INSIGHTS INTO ITS FUNCTION/DYSFUNCTION

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Tau is an intrinsically disordered protein (IDP) found primarily in the axons of neurons. Its aggregation and deposition as neurofibrillary tangles are linked to several tauopathies, including Alzheimer's disease. Additionally, the loss of native interactions between tau and microtubules (MTs) is thought to contribute to pathology. Despite intense study, structural details of the tau-tubulin complex are lacking, in part due to its highly dynamic nature and the capacity to promote tubulin polymerization. Using intramolecular single-molecule Förster Resonance Energy Transfer (smFRET), we determine the topological features of tau bound to soluble tubulin heterodimers [1,2]. Tau adopts an overall extended conformation upon tubulin binding, in which the long-range of contacts between both termini and the microtubule binding region (MTBR) that characterize its compact solution structure are diminished. Surprisingly, the individual repeats within MTBR that directly interface with tubulin undergo an expansion in order to accommodate tubulin binding without changing the overall MTBR dimensions. Notably, it suggests the formation of such a "fuzzy complex", in which tau displays significant flexibility to allow for local changes in conformation while preserving global features. Moreover, our results contrast differences in tau isoforms and a conformational ensemble of tubulin-bound state distinct from its aggregation-prone structure. This work provides insights into the molecular mechanism of tau-mediated tubulin polymerization into MTs and draws attention to the importance of the role of tau's conformational plasticity in function [1].

Acknowledgements

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PHOTOPROTECTION: INSIGHTS FROM THEORY AND EXPERIMENT

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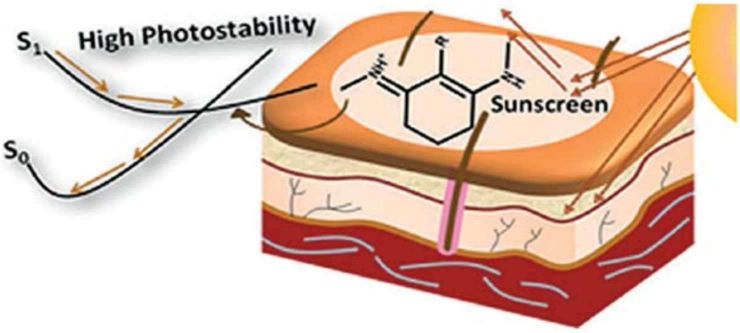
The incidence of skin cancer has been steadily increasing during the last years, and now is the most common type of cancer. This has been related to several reasons, being the increase in sunlight exposure time one of the most relevant. The use of sunscreens has proven of extreme importance in order to prevent the damaging effects of sunlight. These effects could range from just sunburn to skin cancer.[1] There is currently a wide variety of commercial products available in the market, but in most cases the active ingredients that actually prevent the light absorption are only a few. Even more, for the short list of ingredients allowed to be used in different parts of the world, some of them are suspected to have serious concerns about safety regarding both human body and the environment. On the other hand, consumer requirements are increasingly demanding; beyond improved photoprotection, the commercial products are required to have good sensory properties and a prolonged period of action. On top of that, the commercial products are expected to be as environmentally friendly as possible, degrade after use and not bioaccumulate. This long list of requirements make the preparation of new active ingredients for sunscreens a challenging task with profound implications in the field. [2]

During the last years, we have explored by computational means a series of natural occurring compounds known to have excellent properties as sunscreens in biological environments.[3,4] Using the knowledge gathered by the computational study, we were able to design and prepare a series of compounds with very relevant properties.[5]

In this contribution, we will review our efforts in the computational design, preparation and use in real formulations of new compounds that could potentially act as active ingredients in sunscreens.



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AUTOFLUORESCENCE OF PROTEIN AGGREGATES ENABLE *IN-VITRO* SCREENING OF ANTI-AMYLOID DRUGS

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Intrinsic protein fluorescence is typically attributed to the near-UV fluorescence of aromatic amino acids. Surprisingly, recent studies unraveled a visible autofluorescence upon formation of protein crystals and amyloid fibrils[1-3]. This new fluorescence band is excited at the edge of the long UV wavelength range (~ 350 nm) and emits in the deep blue (~ 450 nm). Although several approaches to elucidate the origin of this phenomenon have come forward, the physical mechanism behind it is still under debate [4-5]. Nevertheless, it is recognized that a progressive increase in the fluorescence emission in the visible is concomitant with the growth of amyloid aggregates originated from many different proteins, including the relevant amyloid-β peptide, lysozyme or insulin.

Since the assembly of proteins into amyloidogenic oligomers and fibrils underlies the onset and symptoms of several pathologies, including Alzheimer's disease, Parkinson's disease and type II diabetes, there is a great demand for develop fast and reliable methods for *in vitro* screening of new drugs that may suppress or reverse amyloidogenesis. Our aim is to develop high-throughput assays using a fluorescence plate reader to screen novel anti-amyloid drug candidates based on the autofluorescence of amyloid aggregates. This approach avoid the use of the conventional external dyes such as Thioflavin-T or Congo Red that may perturb the aggregation process or even modify the amyloid binding capacity.

The protein lysozyme was used as a model protein and two known amyloid inhibitors, tartrazine and amaranth[6], were tested. Microscopy gave insights on the number of aggregates and their morphology. The correspondence of steady-state fluorescence and microscopy images confirm that the enhancement in the autofluorescence over time is related to the amyloidogenic aggregation of proteins, and can be detected even in the early self-association stages. The aggregates morphology (size and shape) was related with the presence of amyloid inhibitors. The results from the developed fluorescence plate reader based methodology clearly suggest that fluorescence in the deep blue is a reliable intrinsic probe and can be applied as a first-step screening for amyloid inhibition, providing consistent measures of IC50 values and the rank of drugs efficiency. The *in-vitro* anti-amyloid drugs screening methodology put forward proved to be robust and reproducible. The assays are cell-free, fast to perform and suitable for scaling.

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Quinolimide-based solvatochromic fluorophores

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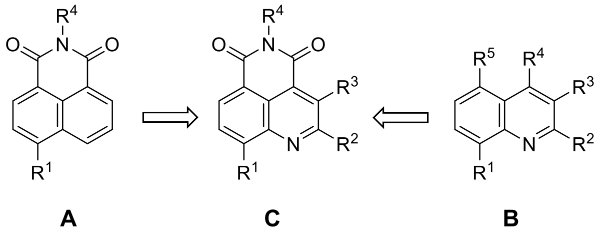
Solvatochromic fluorophores have demonstrated high potential as tools for the study of protein dynamics and protein-binding interactions[1]. In this field, the 1,8-naphthalimide scaffold is found among the most fruitful structures in the design of fluorophores with application in the development of fluorescence biosensors[2]. Considering that introduction of a nitrogen atom into the 1,8-naphtalimide skeleton (**A**) could red-shift the fluorescence emission and increase water solubility, along with the prevalence of the quinoline core (**B**) in diverse fluorescence sensors, we have synthesized and explored the fluorescence properties of chimeric naphtalimide-quinoline fluorophores (**C**)[3]. In this communication we report the design, synthesis and photophysical properties of novel 4,5-quinolimide-based fluorophores, as well as some biophysical applications.



Acknowledgment: The work was supported by the Spanish Ministerio de Economía y Competitividad grants BFU2015-67284-R, and CTQ2014-56370-R.

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PHOTODEGRADATION OF IONIC LIQUIDS: RELEVANT ASPECTS CONCERNING PHOTOCATALYST ACTIVITY

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Ionic liquids constitute a new kind of solvents employed in several industrial activities due to their very particular properties with respect to traditional solvents. However, they are often highly toxic, so that improper use and incorrect disposal lead to important environmental issues.[1]

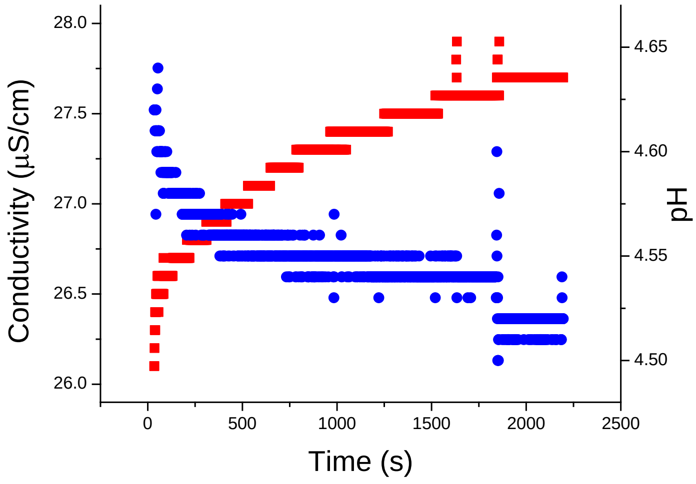
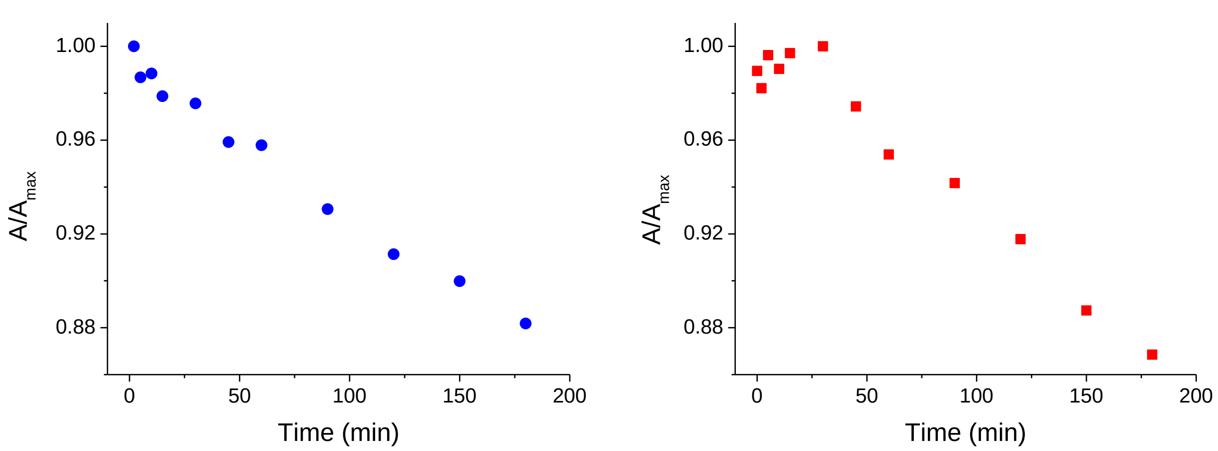


Figure 1. Conductivity (■) and pH (●) change upon adsorption of HPyBr on TiO_2.

NUV/Vis photodegradation of 1-hexylpiridinium bromide (HyPBr) catalyzed by TiO_2 immobilized on different substrates was studied. The interaction of HyPBr with the photocatalyst in the dark showed a conductivity increase coupled with a pH decrease (Figure 1). The effect is fully cancelled out upon irradiation starts. This behavior may arise from a proton release from the hydroxyl groups on TiO_2 surface upon HPyBr adsorption. It is readily neutralized as photodesorption takes place.

Water molecules may also be adsorbed on the surface, but this process revealed much slower. Water adsorption supports the appearing of an induction period in the photodegradation of HPyBr when the photocatalyst is kept wet for a long period (Figure 2).



[D1]

Figure 2. Photodegradation of HPyBr catalyzed by dry (●) and wet (■) TiO_2 immobilized on sand.

Other factors influencing photocatalyst activity have also been studied, such as doping, spatial distribution, or hot air treatment.

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TUNING LUMINESCENCE PROPERTIES AND MORPHOLOGIES IN Au(I) SUPRAMOLECULAR STRUCTURES

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Self-assembly of small molecules by the establishment of non-covalent interactions has received great attention in the past decade as a way to build supramolecular structures with a large number of specific functions and morphologies.[1] As a result, supramolecular chemistry has matured from a conceptually marvelous scientific curiosity to a technologically relevant science encompassing a broad area of advanced materials. Within this field, gold(I) complexes represent an emerging area of investigation in the last years, as they show weak Au(I)···Au(I) interactions which can modulate and govern the resulting assemblies and properties in very different potential applications.[2,3]

The research expertise of our research groups in this field, makes us gaining a denoted expertise on the design, synthesis and characterization of a wide variety of Au(I) supramolecular aggregates. Interestingly, we have observed that the resulting luminescence can be modulated by small modifications on the chemical structure, such as charge or counterion due also to changes on the resulting supramolecular assemblies.

The introduction of the adequate chromophoric units is of great relevance to be able to modulate the aggregation process and, consequently the resulting luminescence, giving rise to the formation of an on/off aggregated/disaggregated systems, easily detected by their different emission.

Spectroscopical characterization by means of NMR, absorption, emission, optical and fluorescence microscopy, SAXS and theoretical calculations have been very useful to understand the systems.[4]

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DNA Intercalators studied by Single-Molecule Fluorescence Techniques

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Small molecules which interact non-covalently with DNA can be classified into three types: intercalators, minor-groove binders and major-groove binders. Intercalators bind to DNA inserting themselves between the base pairs and are used in chemotherapy since they prevent DNA replication. Groove binders are usually sequence specific and constitute potential markers for gene recognition. These different types of interaction must be thoroughly characterized in order to design improved DNA binders. For that aim it is necessary to obtain the complete information about the binding process, not only from a thermodynamic and structural point of view, but also regarding the binding dynamics.

In previous works we studied the interaction of fluorescence labelled bis-benzamidine derivatives as minor-groove binders with DNA hairpins and determined the association equilibrium constants and the corresponding association and dissociation rate constants as a function of the DNA sequence.[1,2] Now we focus on the interaction of intercalators with DNA, choosing the widely-used chemotherapeutic agent Proflavine (PF) and the DNA staining dye Thiazole Orange (TO) as model binders.

We present our studies on the interaction of PF and TO with lambda-DNA (linear double-stranded DNA with 48502 basepairs) as a function of the salt concentration. Using steady-state and time-resolved fluorescence measurements we have determined the stoichiometry and the photophysical properties of the complexes formed between each intercalator and lambda-DNA, as well as the corresponding association equilibrium constants. The presence of dimers and high order complexes is discussed.

From Fluorescence Correlation Spectroscopy (FCS) measurements we have obtained information about the complexation processes of these intercalators and their corresponding dynamics. These data are compared with those previously obtained for minor-groove binders.

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AMINONAPHTHALIMIDE-SQUARAINE DYADS: PHOTOPHYSICAL PROPERTIES AND BIOIMAGING APPLICATION

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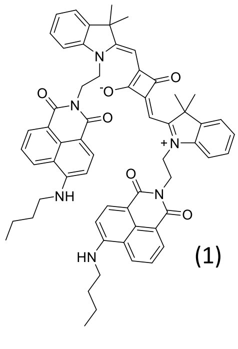
Squaraines is an important part of the cyanine family which have high extinction coefficients, sharp absorption bands, and intense fluorescence spectra in the red and near infrared region in solution.[1] The unique electronic structure and such optical characteristics have made squaraines very attractive for many applications, such as chemosensors, organic solar cells, optical recording media, electro-luminescence diodes, and nonlinear optical devices.[2] 2,3,3-Trimethylindolenine-based squaraines are prepared by the condensation of the heterocyclic quaternary ammonium salts with squaric acid in high boiling point alcohols such as butanol, often in a mixture with aromatic hydrocarbons such as toluene or benzene in order to azeotropically remove the water formed in the condensation reaction (Dean−Stark apparatus).[3]

In this communication, we present a series of aminonaphthalimide–squaraine dyads (1) and (2) that shown squaraine fluorescence sensitization [3]. This was observed upon one- and two-photon excitation of naphthalimide subunits, which extends the application range of the investigated bichromophoric dyads in terms of accessible excitation wavelengths. In comparison with the direct excitation of the squarine chromophore, the two-photon absorption cross-section δ of the dyad (1) is significantly incremented by the presence of the aminonaphthalimide donor.



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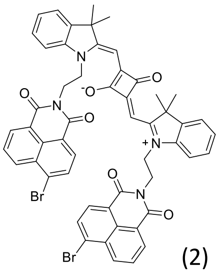

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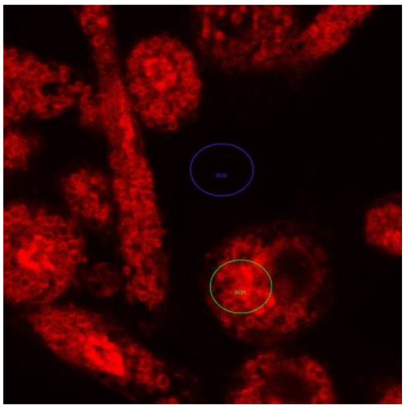

Figure 1

The applicability of the new dyad in the one- and two-photon excitation mode was demonstrated in solution and in a proof-of-principle approach in the fluorescence imaging of HeLa cells (Figure 1).

Acknowledgments: The present study has been supported by MINECO CTQ2016-75870P; by Andalusian Regional Ministry Health (grants: PI-0250-2016); by the European Regional Development Fund (ERDF) and “Plan Propio Universidad de Málaga” (UMA-Andalucía-TECH).

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DYE/SILICA NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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Mesoporous silica nanoparticles are potential drug delivery systems for biomedical applications due to their biocompatibility, tunable size, easy functionalization and high chemical stability. In this work, they will be use as ideal nanocarriers for organic photosensitizers in order to improve their solubility, delivery and targeting to be implement in photodynamic therapy (PDT).

For this purpose, spherical nanoparticles of monodisperse size distribution of around 50 nm are synthesized by Stöber method.[1] Their core-shell structure allows their functionalization with organic molecules of interest. That is a fluorescence dyes in the core (bioimaging), a photosensitizers (PS) in the shell (PDT) [2] together with short chains of polyethylene glycol (PEG) to enhance their stability in water (Figure 1,LEFT). In this regard, different commercial (Rose Bengal or Thionine) and lad-made photosensitizers (based on BODIPY chromophore) with high singlet oxygen quantum yield are tethered to the external surface of the nanoparticles. On the other hand, the amount and the size of the PEG chains are also optimized (MW: 750, 2000 or 5000 Da). As a result, well-dispersed silica nanoparticles with good singlet oxygen production are obtained (Figure 1RIGHT). Finally, "in vitro" experiments are carried out to check their phototherapy activity in HeLa cells, Figure 2.

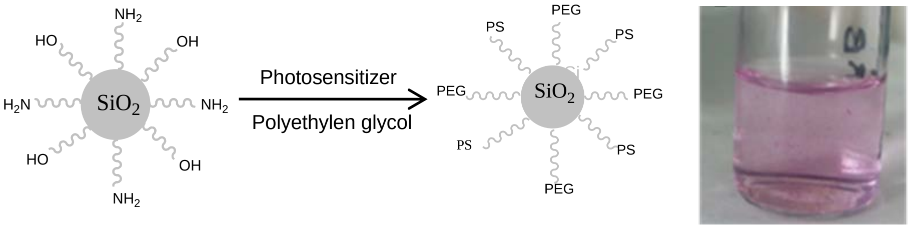

Figure 1: LEFT) Schematic representation of the grafting (PEG+PS) on the external surface. RIGHT) Nanoparticles functionalized with RB and PEG in the shell dispersed in water.

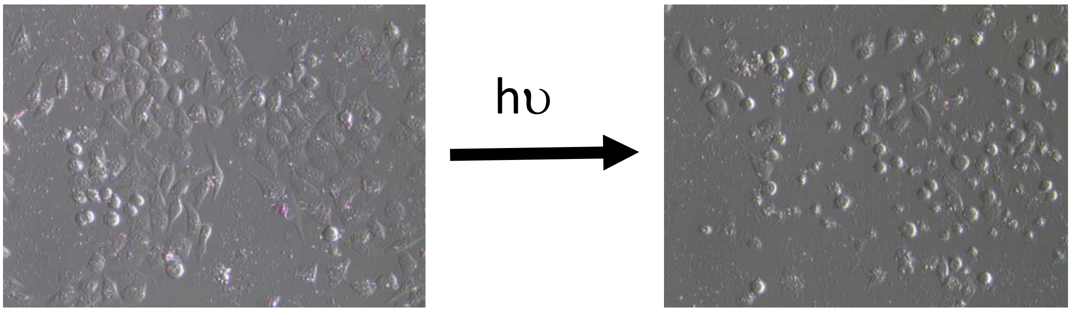

Figure 2: LEFT) HeLA cells after 24 hours incubated under dark. RIGHT) HeLA cells 24 hours after 15 minutes irradiation (λ= 520 nm).

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TUNING SPECTROSCOPIC AND PHOTOREACTIVITY PROPERTIES OF OPTICAL SWITCHES BY EXTERNAL FORCES

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During the last decade it has been shown that mechanical stress can dramatically alter the chemical reactivity of molecular systems, defining the so-called field of covalent mechanochemistry.[1] Nevertheless, most of recent advances deal with thermal (*i.e.* ground state) reactivity, leaving the field of opto-mechanochemistry (*i.e.* excited state) largely unexplored.

Here, we present our latest studies concerning the effects of external forces on spectroscopy and photochemistry of *trans-cis* photoswitches, finally showing that an optomechanical control is indeed possible. Especially, by means of our developed theoretical tools, we evidence how one of the most commonly used photoswitches (*i.e.* azobenzene) can undergo a consistent absorption red-shift when applying elongation forces, as desired in materials science and bio-applications (Figure 1).[2]

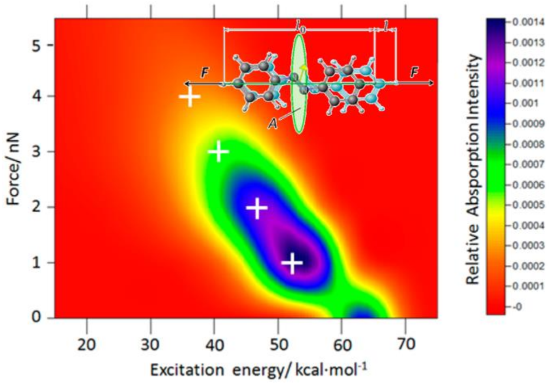

Figure 1. Azobenzene absorption spectrum for different applied elongation forces.[2]

Moreover, the overall photoreactivity of a retinal chromophore model was investigated by multi-configurational non-adiabatic molecular dynamics (NAMD), envisaging a force-induced increase of the photoisomerization quantum yield (Figure 2).[3] This can be rationalized in terms of interplay among the different molecular modes and, eventually, the modification of the conical intersection topology.[4]

Thus, *ad hoc* applied mechanical forces – as predicted by structural and dynamical calculations – can determine novel and/or optimized chromophore properties of interest for future applications in, *e.g.*, polymer science and analytical detection.

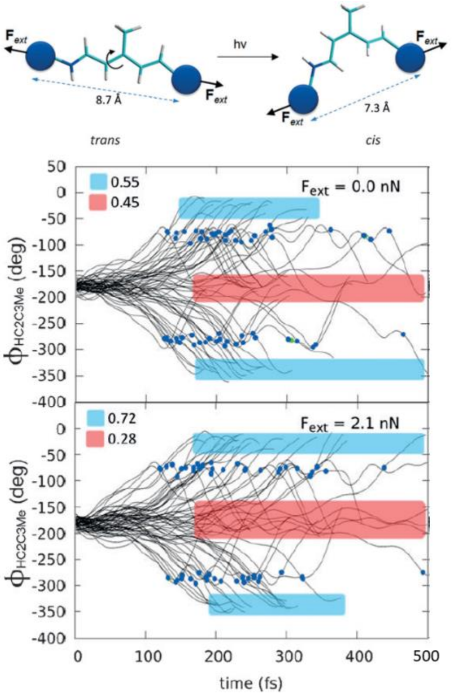

Figure 2. 60 excited state *trans*-to-*cis* NAMD trajectories of a retinal model, without applied forces (55% giving rise to photoisomerization) and with 2.1 nN applied force (72% giving rise to photoisomerization).[3]

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POSTER COMMUNICATIONS

Ba_2SiO_4:Eu^{2+} GREEN PHOSPHOR OBTAINED BY A NEW SOL-GEL ROUTE FOR NEAR-UV EXCITED GREEN OR WHITE-LEDs

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White-light emitting diodes (WLED) can be fabricated by combining blue, green, yellow and/or red phosphors and near-UV emitter diodes, solving the color index and color stability problems usually found in the main white LED commercially available (YAG:Ce^{3+} yellow phosphor and blue LED).[1] One of the challenges concerning this device fabrication is the synthesis of high-efficient near-UV converter phosphors in order to tune the CCT and CRI of the white light.[1] Ba_2SiO_4:Eu^{2+} is a potential candidate to be applied as green component in WLEDs or in green-LEDs used as sources of traffic signals or automotive displays.[2] The quadrilateral area in the Commission Internationale de L'Éclairage (CIE) diagram required for green traffic light application is (0.000, 0.506), (0.224, 0.389), (0.280, 0.450) and (0.000, 0.730), according to the Institute of Transportation Engineers.[2] Additionally, the values required for automotive displays are (0.0137, 0.4831), (0.2094, 0.3953), (0.2879, 0.5196) and (0.0108, 0.7220), according to the Society of Automotive Engineers. [2] Therefore, the aim of this study is to apply an innovative sol-gel route to synthesize a green phosphor based on Eu^{2+}-doped Ba_2SiO_4 phosphor. High-crystalline and monophasic $Ba_{1,97}Eu_{0.03}SiO_4$ was obtained by calcinating a silica xerogel precursor containing both Ba^{2+} and Eu^{3+} cations[3] at 1100 ºC for 10 h under a reductive H_2 (10 %)/N_2 (90 %) atmosphere, decreasing the calcination temperature usually applied to obtain this phase (1200 ºC).[2] In the Ba_2SiO_4 structure, Ba^{2+} ions occupy two sites with coordination number of 9 or 10 and it is expected that Eu^{2+} ions replace Ba^{2+} in the network. The phosphor excitation spectrum is a set of broadbands centered at around 275 nm, 331 nm, 366 nm and 410 nm. Under these excitation wavelengths, the phosphor emission spectra at room temperature display a broadband centered at 505 nm that has been attributed to the Laporte allowed $4f^65d \rightarrow 4f^7$ Eu^{2+} transition. The emission band has the highest intensity under 366 nm excitation. The respective emission spectra measured at 14 K show a broadband with a single Gaussian profile centered at 508 nm. Time-resolved emission spectra measured at 14 K were collected revealing no displacement in the steady-state emission band maximum, when the starting delay (SD) time was changed from 0.01 to 0.03 ms in good agreement with the $4f^65d \rightarrow 4f^7$ Eu^{2+} transition attribution. The lifetime values estimated at room temperature (9.0 ± 0.3 μs) and at 14 K (10.6 ± 0.3 μs) also reinforces the presence of optically active Eu^{2+} ions, rather than the presence of a defect-related component whose lifetime values are typically in the order of nanoseconds. The emission spectrum excited at 366 nm was measured at different temperatures and the emission intensity linearly decreases when the temperature enhances. The band FWHM values also increase when the temperature enhances (39 nm at 14 K and 60 nm at 300 K) due to the thermal quenching at the configurational coordinate diagram. When the temperature increases, the emission maximum has a blue-shift due to the thermally active phonon-assisted tunneling from the excited states of the lowest-energy emission band component to the excited states of the highest-energy emission band component in the configurational coordinate diagram. This observation confirms that Eu^{2+} ions are inserted in two non-equivalent sites in the Ba_2SiO_4 network. Finally, the CIE coordinates of (0.145, 0.564) obtained under 366 nm excitation at room temperature qualify the obtained green phosphor for applications in green-LEDs for use in traffic light, automotive displays or as a green emitter component in near-UV excited white LEDs.

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NEW GENERATION OF IMPROVED PIEZOPHOTONIC MATERIALS WITH INNOVATIVE FUNCTIONALIZED CARBON NANOTUBES

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Excitation of highly absorbing molecules and materials whose deactivation pathways are mainly non-radiative leads to the release of heat into the surrounding environment. Depending on the characteristics of the laser excitation source and target material, the fast release of the energy obtained by light excitation gives rise to two main types of pressure waves: shock waves and photoacoustic (PA) waves. Shock waves are generated by dielectric breakdown and material ablation, when the laser optical power density is above thermal threshold of the target material. Those waves are characterized by an abrupt discontinuous change in the material properties that propagates at a supersonic speed and induces a high increase in the temperature and pressure of the traversed medium [1]. We work with PA waves that are produced by thermoelastic expansion of a confined material. In the absence of a change of state the transient heating of the material surface is the dominant mechanism of acoustic generation. PA waves propagate into the materials at the speed of sound with moderate rise in system pressure but with short rise times and broader wave bandwidths [1,2].

The unique characteristics of the PA waves, especially the high frequency of the generated waves, have enabled us to develop innovative technologies in the field of photoacoustic gene transfection [3]. An excellent example of the distinctive character of these photoacoustic waves was shown when we used them to enable the transfection in 10 minutes of a plasmid DNA encoding Green Fluorescent Protein (gWizGFP, 3.74 MDa) in COS-7 monkey fibroblast cells with an efficiency of 5% at 20 °C and without significant cytotoxicity under these conditions [3].

We used materials that were developed to convert nanosecond laser pulses into PA waves capable of permeabilizing the stratum corneum and enhance transdermal drug delivery [2]. We have recently developed efforts to create new and more efficient piezophotonic materials (which convert light “photonic” into pressure waves “piezo”), optimized for picosecond laser pulses PA waves generation with higher pressure ranges and higher broadband frequency. In this work we present for the first time the results of our new functionalized carbon nanotubes that strongly absorb radiation ($\mu a > 2000$ cm–1) and rapidly dissipate the excess energy into heat, conjugated with polymers that have a high thermal expansion coefficient. The preliminary results are encouraging and show PA waves with improved profiles.

These new materials will generate intense, broadband ultrasound pulses with wavelengths commensurable with cell dimensions and we anticipate those pressure gradients will be capable of substantially increase transfection efficiency without added toxicity.

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EFFECT OF THE CONCENTRATION ON THE EMISSION FEATURES OF COLLOIDAL SOLUTIONS OF SILICON NANOPARTICLES AND APPLICATION AS PRIMARY LUMINESCENT THERMOMETERS

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Colloidal solutions of luminescent nanoparticles (NPs) are systems required or advantageous for applications in the field of biomedicine,[1] nanothermometry,[2] and in material processing techniques as roll-to-roll film deposition that enables large area films for production of optoelectronic devices (*e.g.* solar cells, light-emitting diodes and photodetectors).[3]

In this work, a photoluminescence study was performed on colloidal solutions of organically functionalized silicon nanoparticles with several concentrations to understand how the concentration impacts on the light emission features of these systems and evaluate the performance of these systems as luminescent primary thermometer. The dynamic light scattering measurements show evidence that the colloidal solutions are monodisperse with an agglomeration that do not depend on the concentration of the solution. The emission spectra and the emission decay curves are also almost independent on the concentration and the quantum yield increases with the increase of the solution concentration. The evaluation of the colloidal solutions of Si NPs as thermometer show that the operation is robust regarding the change in the excitation wavelength, for the studied temperature range (293-343 K). Independently on the excitation wavelength, the thermometric parameter, that is the emission peak position, is predicted by the Varshni's law, making this a primary thermometer. The relative thermal sensitivity and the temperature uncertainty are ≈0.03 %.K^{-1} and ≈4 K, respectively.

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STUDY OF AGGREGATION OF L & H APOFERRITIN SUBUNITS BY USING FLIM MICROSCOPY

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One of the most serious biomedical challenges at the moment is the dynamic, functional and structural characterization of the intermediates involved in the mechanism of formation of amyloid fibrils [1]. The aberrant aggregation of certain proteins into β-sheet-rich fibrillar plaques is the main molecular hallmark of a family of diseases, such as Alzheimer´s and Parkinson´s disease. The early stages of such aggregation occur through the formation of non-specific contacts between monomers, which finally result in the growing nuclei.

In a previous work, we employed single-molecule Fluorescence Lifetime Imaging Microscopy (FLIM) to study the intra-oligomer fluorescence resonance energy transfer (FRET) in the aggregation of fluorescently-labelled ferritin, a key component of the iron regulatory system in the brain and thus being recognized as a crucial protein related with some neurodegenerative disorders. Our FLIM-FRET experiments allowed us to study the soluble oligomeric intermediates at the molecular level, contributing to a new vision of such heterogeneous system [2].

In this work, we have focused our attention to apoferritin, a transmembrane protein which captures iron and introduces it inside the cell. This protein is formed by two well-defined subunits, H (heavy) and L (light). By using Atomic Force Microscopy we found changes in the chirality and morphology of amyloid fibrils, depending on whether they were formed only by H subunits or L subunits. Therefore we have studied the first stages of the aggregation of H- and L- apoferritin by using FLIM-FRET microscopy with molecular resolution [3].

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OPTICAL LIMITING PROPERTIES IN THE FEMTOSECOND REGIME OF AN ALUMINUM PHTHALOCYANINE AND ITS IRON OXIDE NANOPARTICLE COMPOSITE

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High intensity laser light sources have become more and more normal in the working and daily environments. The protection of delicate optical instruments and of human organs, especially the human's eyes, from high intensity laser beams led to the development of the field of optical limiting materials. An efficient optical limiting material (OLM) has high-transmittance for low-intensity light while strongly attenuate intense and potentially dangerous laser beams. In most cases, molecular sequential multiphoton absorption is the mechanism behind the appearance of nonlinear optical effects and leads to be observation of nonlinear transmission, which can be used in optical limiting devices.

Phthalocyanines provide a suitable molecular basis for the production of efficient optical limiting materials. Their nonlinear optical (NLO) properties can be modified via appropriate combination and modulation of several structural components,[1,2] namely by varying the electronic configurations in a controlled fashion through peripheral substitution, by variation of the central atom or axial ligand modification. Additionally, attempts to enhance NLO properties performances by tethering these types of organic macrocycles to nanomaterials has been a recent strategy employed by many researchers.[3,4] We report the first synthesis, spectroscopic characterization and nonlinear optical properties, namely OLM behavior in solution, of a hybrid organic-inorganic material, based on magnetic iron oxide nanoparticles tethered with aluminum phthalocyanine, through axial conjugation (Figure 1). Studies were performed on the femtosecond laser regime at the green (532 nm) and red (800 nm) spectral regions. The measurement of optical limiting properties done was based on the open-aperture Z-scan method.[2,4]

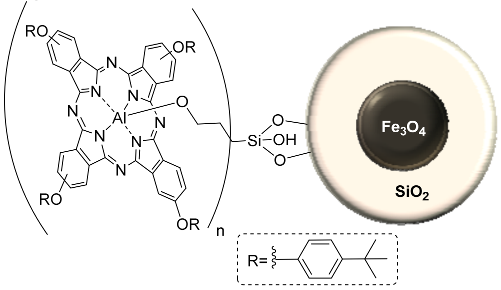

Figure 1- Structure of the magnetic iron oxide nanoparticle tethered with aluminum phthalocyanine.

A significant transmission drop was observed for both complexes with increasing incident laser fluence, at both working wavelengths. This decrease of optical transmission indicates that the studied compounds behave as reverse saturable absorbers, with the reversible formation of excited states having larger absorption coefficients than the original ground state, this happening upon increase of the incident light intensity. The experimental transmittance drop reaches significant values, indicating that the studied molecules have potential as OLM. The observed low limiting threshold of the hybrid organic-inorganic material indicates that the presence of the magnetic nanoparticle counterpart as axial ligand with respect to the aluminum(III) metallophthalocyanine is beneficial for the improvement of the nonlinear transmission properties. This suggests that the nonlinear optical properties are dependent on the capability to prevent intermolecular aggregation.[5]

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AGGREGATION INDUCED EMISSION IN PHENOTHIAZINE -TPE AND -TPAN POLYMERS

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The great majority of luminogens are emissive in dilute solutions while they are weakly fluorescent or even non-emissive in the solid state or in concentrated solutions. Under some circumstances this is a phenomenon known as aggregation-caused quenching (ACQ). Contrary to the ACQ effect, some luminogens are non- or weakly emissive in dilute solutions but become highly emissive upon aggregation in poor solvents or in the solid state. This observation lead in 2001, by Tang and co-workers to coin this a phenomenon as aggregation-induced emission (AIE)[1]. The mechanisms proposed for this phenomenon involve restriction of molecular motions (RIM), formation of J-aggregates and suppression of the charge-transfer (CT) state.[2] AIE materials have been widely applied in various fields, including as organic light- emitting diodes (OLED) devices and as chemo- and bio-sensors.[3] Our group have successfully characterized the AIE effect in polymers(2,3,3-triphenylacrylonitrile, TPAN), which exhibits so-called crystallization-induced emission (CIE) and was used for constructing AIE-active luminophores, that were attached to the backbone of electron-rich polycarbazoles and polytriphenylamines, thus designing donor-acceptor-type polymers.[4] In this work, two phenothiazine based polymers: tetraphenylethylene- (PTzTPE) and triphenylacrylonitrile-substituted (PTzTPAN) polyphenothiazines have been investigated in solid state, organic solvents and THF:water organic mixtures, to induce aggregation. The PTzTPAN was found non-fluorescent in pure solvents and weakly fluorescent even when aggregated (ϕ_F= 0.01in 10%THF/90% water), whereas with PTzTPE an increment of the total emission is observed when the fraction of water in THF:water mixtures is increased: the ϕ_F increases form 0.06 in THF to 0.12 in 10%THF:90% water. An increase in the ϕ_F with the addition of a poor solvent, in this case water, was attributed to AIE effect (**Figure 1**).

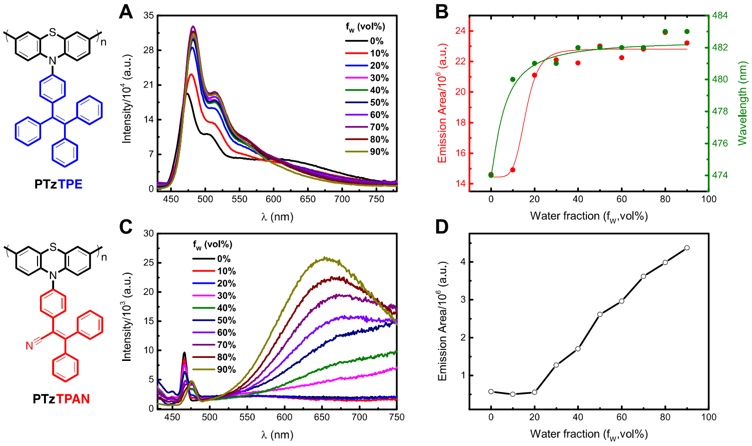

Figure 1. Fluorescence emission spectra of PTzTPE (A) and PTzTPAN (C) in THF/water mixtures with different water content; and emission maxima and emission area of PTzTPE (B) and emission area of PTzTPAN (D) with increasing water content.

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ANTRAQUINONES AS ELECTROLYTES FOR REDOX FLOW BATTERIES: A COMPREHENSIVE SPECTRAL, PHOTOPHYSICAL AND ELECTROCHEMICAL STUDY

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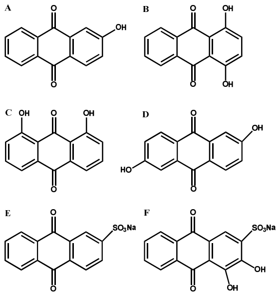
Organic aqueous flow batteries have been recently been proposed as a low-cost and an alternative to the present metal-based redox flow batteries(RFBs) technology [1–4]. The envisioned features of using organic redox species are low cost and increased flexibility with respect to tailoring redox potential and solubility from molecular engineering of side groups on the organic redox-active species. A study of the electronic spectral and photophysical properties of anthraquinonoid type structures obtained in water at different pH values, Scheme 1, together with their electrochemical characterization as electrolytes has been undertaken.



Scheme 1 – Anthraquinonoid type structures: A) 2-hydroxyanthraquinone, B) 1,4-dihydroxyanthraquinone, C) 1,8-dihydroxyanthraquinone, D) 2,6-dihydroxyanthraquinone, E) anthraquinone-2-sulfonic acid and F) 3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid.

The study includes absorption and emission spectra together with quantitative measurements of the deactivation of the first excited singlet state, from which the rate constants for all the decay processes has been obtained. The oxidation and reduction mechanisms will be discussed. With selected electrolytes a prototype of all-quinone based RFB will be presented.

Acknowledgments

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SUSTAINABLE LIQUID LUMINESCENT SOLAR CONCENTRATORS

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With the expected need of using renewable energy sources over fossil fuels, much more attention has been given to alternative methods of getting electrical energy in a sustainable way. Solar energy is one of the renewable energy sources with higher potential. In this scope, photovoltaic (PV) cells play a crucial role in harvesting solar energy and converting it to electricity, and this is a technology in continuous development.[1] Nevertheless, there are some challenges to be addressed, namely i) PV devices efficiency increase by, for instance, reducing the mismatch between their spectral responsivity and the AM1.5G solar spectrum, ii) reduction of the environment impact through, for instance, the reduction of PV cells size or PV urban integration and iii) sustainability by using nature-based materials.[2]

Luminescent solar concentrators (LSCs) appear as a solution to cope with the mismatch between solar cells response and the solar spectrum,[3] with the additional advantage of facilitating the integration of photovoltaic devices into the urban environment, since they can be embedded in building façades and windows. Moreover, the fact of LSCs being able to concentrate sunlight, enables the fabrication of smaller PV devices, with less active area and, consequently, less amount of PV material needed, which will allow to decrease the environmental impact arising from PV harvesting technologies.

The search for new materials to be applied in LSCs and inserted in a sustainable urban development is, nowadays, a priority with the main goal of reducing the cost of electricity and solar energy harvesting, preferentially, with the use of natural and sustainable materials, with minor environmental impact.

In this work, the R-phycoerythrin (R-PE) protein, which is one of the most abundant phycobiliproteins in red macroalgae, was used as optically active center for LSC applications. In this case, the R-PE was extracted from marine biomass, namely fresh Gracilaria sp. red algae by an extraction and purification method which does not affect its conformational structure or chromophore structural integrity. We should note that the use of Gracilaria sp. algae takes advantage of local resources, since it is abundant in Ria de Aveiro, Portugal.[4]

The R-PE was used dispersed in aqueous solutions making this approach totally sustainable and without waste nor significant negative impact towards the environment. Solution with different R-PE concentrations ranging from 4.2×10^{-8} to 1.7×10^{-6} M, with high molar brightness values (2.2×10^{5} to 6.2×10^{5} $M^{-1}\cdot cm^{-1}$) were fully characterized in terms of optical properties and used to fabricate LSCs. Also, a planar LSC and a bundle structure of cylindrical LSCs, made of a glass cuvette and hollow-core plastic optical fibers, respectively, which were filled with the R-PE aqueous solutions were fabricated. The performed electrical measurements in coupled c-Si PV devices, resulted in maximum optical conversion efficiency values of ~5.6% (planar) and ~2.7% (bundle), and power conversion efficiency values of ~0.3% (planar) and ~0.02% (bundle).

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CONJUGATED POLYMER-DI-UREASIL ORGANIC-INORGANIC COMPOSITES FOR OPTICAL AMPLIFICATION

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White light-emitting diodes (LEDs) are emerging as a cost-efficient alternative solution to wireless communications, namely visible light communications (VLC) [1]. As white LEDs use a combination of a yellow emission combined with the faster response of a blue-emitting LED, VLC technology requires an optical amplification in the blue spectral region to improve the signal-to-noise ratio [1]. We report the fabrication and characterization of waveguides based on di-ureasil organic-inorganic hybrids incorporating a blue-emitting poly(fluorene) conjugated polyelectrolyte, namely, poly[9,9-bis(4-sulfonylbutoxyphenyl) fluorene-2,7-diyl-alt-1,4-phenylene] (PBS-PFP) for optical amplification in VLC. The incorporation of PBS-PFP led to an enhanced emission in the blue spectral region (390-550 nm), that overlaps that of commercial LEDs. Moreover, the high absolute emission quantum yield values facilitate the excitation of the waveguide using a UV LED [2].

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EXFOLIATED GRAPHITIC CARBON NITRIDE FOR PHOTOCATALYTIC DEGRADATION OF AROMATIC CONTAMINANTS WITH SIMULTANEOUS PRODUCTION OF H_2O_2

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Graphitic carbon nitride (g-C_3N_4) has recently attracted a huge interest in heterogeneous photocatalysis, because of its favourable optical semiconductor properties, ease of preparation and flexible possibilities of functionalization. In addition, this material can be activated by the visible part of the electromagnetic spectrum for the efficient removal of organic compounds from water. Many recent reports are however centred in the study of model systems using dyes as parent organic substrates [1-3]. Our study aims to elucidate the mechanism involved in the photocatalytic degradation of phenolics dissolved in water.

A thermally-exfoliated g-C_3N_4 material (gCN$_T$), synthetized as described elsewhere [4] was used in the photocatalytic experiments with specific light emitting diodes (LEDs) sources having a maximum emission wavelength at 417 nm. The performance on degradation of different phenolic compounds (considering the order, nature and position of the substituent) typically found in contaminated aqueous effluents was evaluated in aqueous model solutions. Because hydrogen peroxide was formed during organics conversion, both concentrations were followed, as well as the total organic carbon (TOC) content of the solutions. As an example of the results to be presented, we can see that nearly 100 % of the parent phenol conversion was achieved in the photocatalytic experiments using gCN$_T$ (Fig. 1). It is visible that the amount of H_2O_2 reaches a maximum (ca. 2.0 mmol L^{-1}) at 60 min. Moreover, nearly 80 % of TOC abatement was achieved by the end of the experiment, the remaining being due to the formation of low molecular weight carboxylic acids.

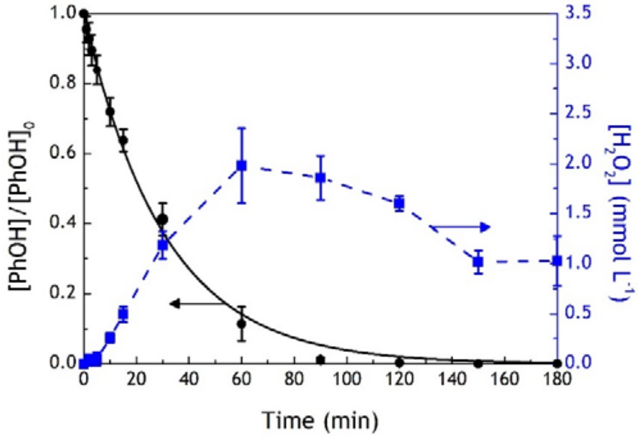

Figure 1. Phenol normalized concentration and H_2O_2 production during photocatalysis (0.50 g L^{-1} catalyst load).

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TUNING UP THE SENSITIVITY OF UPCONVERTING NANOTHERMOMETERS

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The hasty progress in smart, portable, flexible and transparent integrated electronic and optoelectronic technology is clearly one of the driving forces in nanomaterials science. New approaches combining transparent conducting electrode materials and upconverting nanocrystals are being envisaged for the next-generation of optoelectronic devices.[1] The recently recognized critical role of the dimensions of upconverting nanocrystals opened the possibility to engineering its emission skills in specific circumstances.[2] Additionally, we recently reported a straightforward method to predict the temperature calibration curve of any upconverting thermometer based on two thermally-coupled electronic levels,[3] demonstrating that these systems are intrinsically luminescent primary thermometers, avoiding time-consuming calibration procedures.

In this work we report nanocomposite transparent films combining a poly(methyl methacrylate) (PMMA) matrix and a percolating network of Ag nanowires upconverting nanoparticles of distinct sizes and compositions are excellent platforms to thermally fine-tune the particles' emission intensity (Figure 1A). Using large (300 nm x 160 nm) Yb^{3+}/Er^{3+}-doped nanocrystals as a reference primary thermometer, the Yb^{3+}/Tm^{3+}-doped nanoparticles (diameter of 6.6 nm) thermal response was calibrated. Using a ratio of intensities between the Er^{3+} and Tm3^{+} transitions, it results a relative thermal sensitivity of 4.3%·K^{-1} at 320 K, a value that corresponds to more than 4-fold improvement relatively to that reported so far for upconverting nanoparticles based on thermally coupled levels at the same temperature (*e.g.* 0.9·%·K^{-1}).

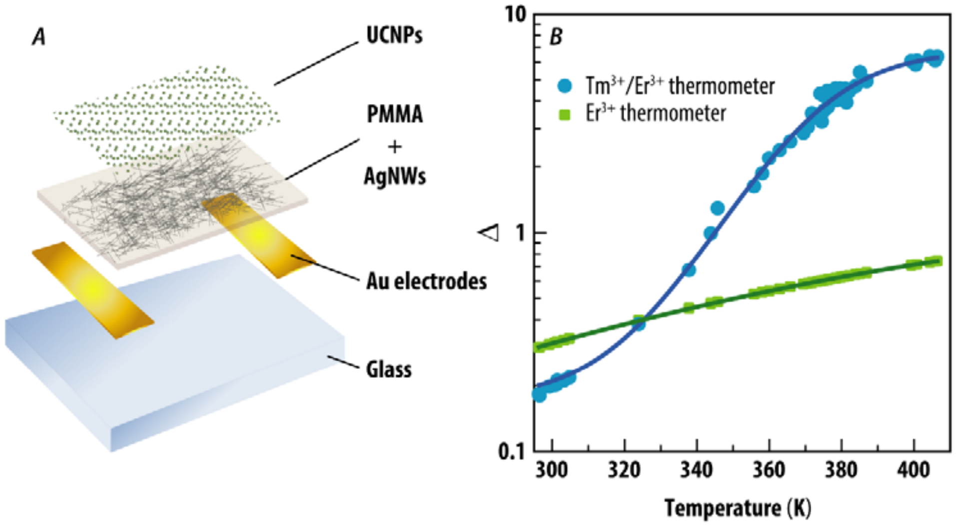

Figure 1. (A) Schematic of the nanocomposite transparent films combining a PMMA and a percolating network of Ag nanowires upconverting nanoparticles. **(B)** Temperature dependence of the intensity ratio Δ involving Tm^{3+} and Er^{3+} transitions (blue) or two transitions of Er^{3+} (green).

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MEASURING THE QUANTUM YIELD OF LN^{3+}-DOPED NANOPARTICLES IN THE NIR SPECTRAL REGION

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The emission quantum yield values of upconverting and downshifting nanoparticles are very often not reported in the literature, despite of its importance for characterizing the material's performance. The main reasons for that are related to the quite expensive setups and consequential laborious procedures to perform experimental measurements, in particular when the emission or the excitation bands are in the near-infrared (NIR) spectral range of the electromagnetic spectrum. Most of the emission quantum yield values reported so far for upconverting nanoparticles with excitation in NIR refer to $NaYF_4$:Yb^{3+}/Er^{3+}, that, depending on the synthesis method, solvent, particle's size and concentration, can vary almost two orders of magnitude.[1] For downshifting nanoparticles, the widely reported Ln^{3+}-based systems emitting in the NIR are based in Nd^{3+} although some the Er^{3+}-doped examples very often presents the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ band at 1550 nm.

Here, we report the measurement of the downshifting emission quantum yield in the NIR spectral range of $NaErF_4$:Ce and $NaErF_4$:Ce@$NaYF_4$ nanoparticles (prepared in Harbin Institute of Technology) in aqueous suspensions using a recently available experimental setup (Quantaurus-QY Absolute PL quantum yield spectrometer, Hamamatsu)[3]. Besides the quantum yield values dependence on the excitation power density, the photothermal heat efficiency of the same particles was quantified using the same equipment, following the strategy reported in the literature.[4]

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ON THE HIGH PHOTOSTABILITY OF INDIRUBIN

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Indirubin and indigo are the core representatives of a rather small category of bis-indole alkaloids belonging to the family of indigoids. Indirubin is one of the structural isomers of indigo and in the (red) shadow of this compound. Its relevance (besides the red tone that it imparts to indigo denims) is linked to the use, known for millennia, in traditional Chinese medicine, as one of eleven components of *Danggui Longhui Wan,* a medicine for the treatment of Leukemia.[1]

In Indigo, as with indirubin, the excited state deactivation is known to be dominated by radiationless processes (the internal conversion quantum yield is >99.9%).[2] In indigo the mechanism is associated to a fast intramolecular (single) proton transfer.[3] The excited state mechanism involves the formation, by light excitation, of an instantaneously formed keto form which proton transfers to an enol form that decays to the ground state.[4]

In this work indirubin was investigated by both steady-state and transient (time-resolved fluorescence and fs-TA) techniques, together with TDDFT calculations aiming to further understand the mechanism behind this extremely efficient non-radiative process.

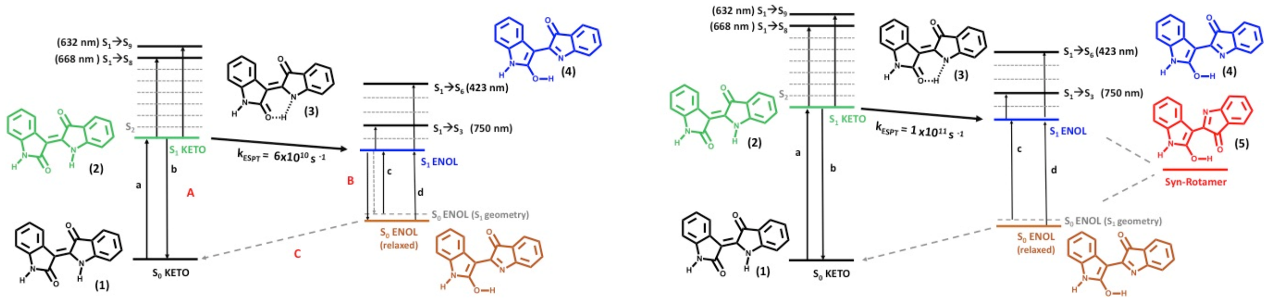

Fig. 1- Illustrative scheme for the excited state deactivation of Indirubin in glycerol (left) and methanol (right). The capital letters A, B and C are linked to the decays in Fig. SI1. (a) $S_0 \rightarrow S_1$ absorption, (b) $S_1 \rightarrow S_0$ emission, (c) S_0 (enol)$\rightarrow S_1$(enol) (the geometry is maintained) and (d) S_0 (enol, relaxed)$\rightarrow S_1$(enol). The attribution of the transitions is established from TDDFT calculations.

In comparison with indigo, indirubin shows a more efficient radiationless deactivation and consequently a high stability towards light. Whereas the highly efficient dark deactivation process in indigo is linked to a single excited state proton transfer, with indirubin in non-viscous solvents, such as methanol and 2MeTHF, an additional pathway exists involving rotation between the two indole-like moieties. This leads to a syn-conformer having a more efficient radiationless deactivation pathway. The mechanism is inhibited in the viscous solvent glycerol.

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MONO-AND DI-SUBSTITUTED INDIGO DERIVATIVES: SYNTHESIS AND EXCITED STATE CHARACTERIZATION

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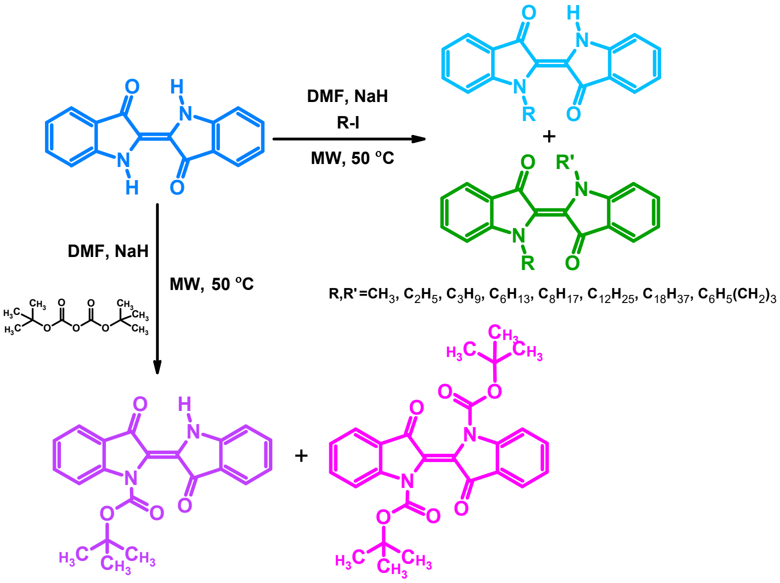
Indigo and its derivatives are included in the most ancient and popular natural dyes.[1] The longevity of indigo is chemically related to its photostability which is linked to an excited state proton transfer.[2] Structural changes in the structure of indigo may tune its photochemical and photophysical properties. Modifications in the chromophoric core (the H-chromophore), following the methodology reported by Setsune[3], have been accomplished by replacing one or two N-H groups by different groups, see **Scheme 1**. In the present work mono-and di-substituted indigo derivatives have been synthesized and their electronic spectral and photophysical properties investigated in different solvents in order to study the influence of the mono- and di-substitution in the photophysical and photochemical properties of indigo.



Scheme 1. General synthetic procedure followed by the synthesized indigo derivatives.

A comprehensive photophysical study involving determination of the fluorescence quantum yields and lifetimes (from time resolved fluorescence and fs-TA data) will be presented in solvents of different polarity and viscosity. It will be shown that the mono- or di-substitution and the size of the alkyl chain influences the photophysical properties of the compounds. Trans-cis photoisomerization it was found present with the di-tBOC substituent and found absent with all the others compounds.

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GOLD NANORODS FUNCTIONALIZED WITH FLUORESCENTLY-LABELED DNA'S: A SINGLE-PARTICLE SPECTROSCOPY STUDY

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Metal nanoparticles can be used as plasmonic antennas to couple light more efficiently in the excitation and emission from fluorescent dyes [1]. This feature has been explored for the development of plasmon-enhanced fluorescence biosensors by increasing response signals that are triggered by molecular recognition events [2,3]. Here, we report on the functionalization of gold nanorods with fluorescently-labeled DNA hybrids, or with molecular beacons, in order to evaluate antenna effects for fluorescence emission enhancement. Firstly, the top emission enhancements were evaluated on glass-immobilized single nanorods interacting with ATTO647N-labeled DNA hybrids in aqueous solution. This study revealed top enhancements for single-molecule fluorescence in the range of a hundred-fold (Figure 1), which agree with theoretical simulations. Larger emission enhancements are eventually possible in nanodimer antennas [4]. In the second part of the work, gold nanorods were functionalized in colloidal solution with a large number of molecular beacons that have ATTO647N dye for fluorescence detection of oligonucleotide sequences proposed as biomarkers for targets such as dengue virus, sleeping sickness and cancer. The gold nanobeacon assemblies were characterized by measurements of zeta potential, UV/Vis absorption and fluorescence correlation spectroscopy. This platform can provide miniaturization, label-free and real-time detection, being a promising fluorescence signaling tool to improve biosensor responses for the purpose of clinical diagnostics.

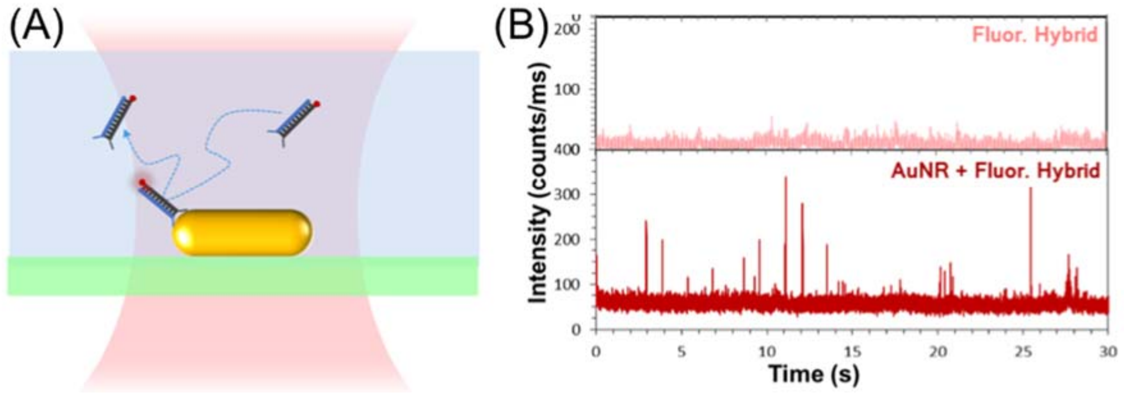

Figure 1: (A) Scheme of the experiment of fluorescence enhancement that depicts DNA hybrids labeled with ATTO647N dye (red circle) in solution diffusing around a gold nanorod. (B) Emission intensity time traces: (top) from a region of the surface without any particle, but in the presence of ATTO647N-labeled DNA hybrids, and; (bottom) from an individual gold nanorod in the presence of ATTO647N-labeled DNA hybrids in solution. The latter shows strong bursts of fluorescence emission due to events of plasmon-enhanced fluorescence from the interaction of fluorescently-labeled hybrids with a single gold nanorod.

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N-BODIPY Dyes; Privileged Scaffold to Develop Photonic Materials

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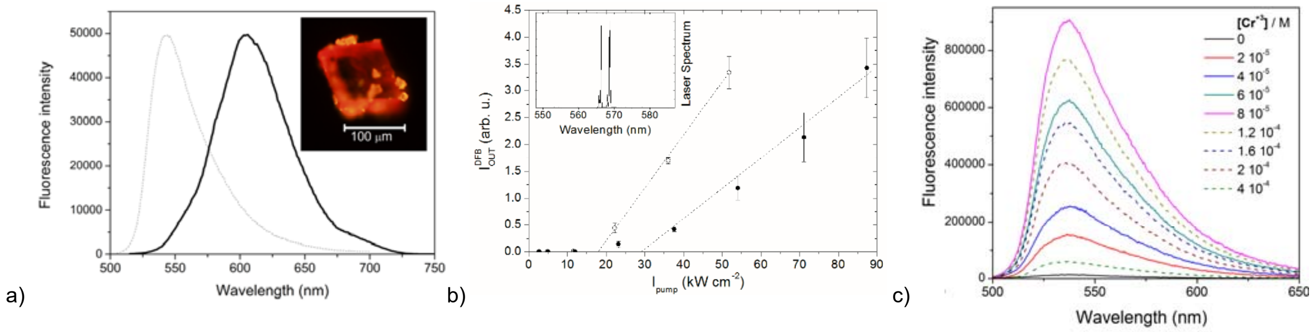
N-BODIPYs (diaminoboron dipyrromethenes) are unveiled as a new family of BODIPY dyes with huge technological potential. In the herein project it have been possible the replacement of strongly electronegative fluorine atoms by nitrogen atoms. Synthetic access to these systems has been gained through a judicious design focused on stabilizing the involved diaminoboron chelate. Once stabilized, the key diaminoboron group of the N-BODIPYs opens up novel avenues for multifunctionalization towards the design of smart dyes with applications in appealing technological fields, ranging from lasing to chemosensing.[1] Indeed, the photophysical signatures of these novel compounds depend markedly on chemical modifications around the nitrogen atoms of their diaminoboron moieties. Thus, stabilized N-BODIPYs based on tosylated amines, spiranic or not, give rise to bright fluorophores even in the solid crystalline state (Figure 1a), with notable lasing capacities in the liquid phase (surpassing 60% laser efficiencies) or doped into polymers (solid state dye lasers), improving the laser performance of their commercial counterpart PM567 (Figure 1b). In contrast, the sole arylation of the spiranic diaminoboron moiety (benzene fusion) activates a photoinduced electron transfer (PET) process that effectively quenches the fluorescence response of the dye. The reliability of such a pathway has been predicted theoretically, and supported experimentally by the recorded increase in fluorescence emission upon the addition of cations with high charge density. This fluorescence sensitivity makes the described benzo-fused spiranic N-BODIPYs quite useful as cation sensors,[2] especially for protons and Cr^{3+} ions (Figure 1c).



a) b) c)

Figure 1. a) Fluorescence image of a representative crystal and its fluorescence spectrum in diluted solution (dashed line) and in the solid state (bold line) upon irradiation at 470 nm. b) Light–light curves for the solid-state distribute feedback laser (DFB) emission of N-BODIPY (hollow circles) and PM567 (filled circles). c) Fluorescence spectra corresponding to the titration of dilute ethanolic solutions of N-BODIPY (dye concentration $4 \cdot 10^{-6}$ M) with representative Cr^{3+} cation. The spectra in dashed lines are those in which the fluorescence intensity starts to decay with the cation concentration.

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g-C_3N_4/Zn_2Al-LDH 2D/2D HETEROJUNCTION FOR LIGHT-INDUCED PHOTCATALYTIC HYDROGEN EVOLUTION

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The current energy crisis requires the development of novel technologies for the sustainable production of energy (H_2). The construction of heterojunctions by combining two different semiconductors (SC), particularly two-dimensional (2D) layered architectures with suitable conduction and valence band potentials is one of the most effective approaches to enhance the separation efficiency of photogenerated charge carriers during the photocatalytic process [1]. Layered double hydroxides (LDHs) are layered anionic clays, with general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{z+}(A^{n-})_{z/n}.yH_2O$, and consist in positively charged layers with divalent M^{II} and trivalent M^{III} metal cations (Cr, Zn, Al, Cu, etc.), octahedrally surrounded by oxo bridges and OH groups, equilibrated by the presence of interlayer anions and water, in order to maintain overall charge neutrality [2,3]. Owing to their unique layered structure, compositional flexibility and structural morphology, LDH are attractive as a SC photocatalyst [3] to couple with layered graphitic carbon nitride (g-C_3N_4) [4]. g-C_3N_4 is a SC with a band gap of 2.7 eV, corresponding to an optical visible light wavelength of 460 nm, with suitable electronic band structure for photocatalytic H_2 evolution [5,6].

We report the synthesis of a hybrid heterojunction coupling g-C_3N_4 with Zn_2Al-LDH, through a facile impregnation method for water splitting towards H_2 evolution. The structural, optical, and morphological properties of the hybrid have been characterized by different physicochemical techniques. Its photocatalytic activity was evaluated under UV-vis and visible light irradiation in the presence of a co-catalyst (Pt) and of a sacrificial donor (CH_3OH, EDTA and TEOA). The photocatalytic activity of g-C_3N_4/Zn_2Al-LDH was $\sim$ 2 times higher compared to pure Zn_2Al-LDH when using EDTA as sacrificial agent. The enhanced photocatalytic performance could be ascribed to the synergistic effect between Zn_2Al-LDH and g-C_3N_4, in which the dispersion of g-C_3N_4 over the brucite layer of LDH results in the reduction of the electron-hole recombination, thus increasing the charge carrier efficiency and promoting the photochemical water reduction.

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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF NEW BODIPYs FOR BIOIMAGING

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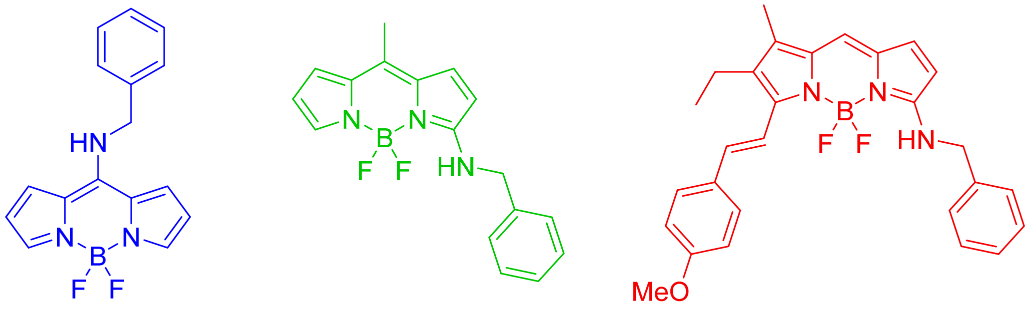
New boron dipyrromethene (BODIPY) dyes substituted with a benzylamino group have been synthesized, Scheme 1. Position of substituent has a strong influence in their spectropic properties [1] and the benzylamino group position modifies the spectral band wavelength, the fluorescence quantum yields, and lifetimes [2]. Whereas the 8-benzylamino derivative **(2)** emits in the blue range, the 3-substituted **(4)** shows green fluorescence. Additionally, the extension of the conjugation at the 5-position of 3-benzylaminoBODIPY **(6)** produces a bathochromic shift of the absorption and emission spectra resulting in red fluorescence. The solvent effect on their spectroscopic properties has been investigated and analised using the generalized Catalán solvent scales. Quantum-chemical calculations have been performed to assess the effect of the substituted position on the spectroscopic properties of BODIPYs. Besides, the BODIPY dyes have been employed as probes in fluorescence lifetime imaging (FLIM) of living cells, demonstrating their potential for bioimaging.



2 **4** **6**

Figure 1 .- Structures of the blue (2), green (3) and red (6) benzylamine-substituted BODIPYs synthesised.

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A COMPREHENSIVE INVESTIGATION OF THE INTERACTION OF A 7-HYDROXYCOUMARIN DERIVATIVE AND CUCURBIT[7]URIL IN WATER

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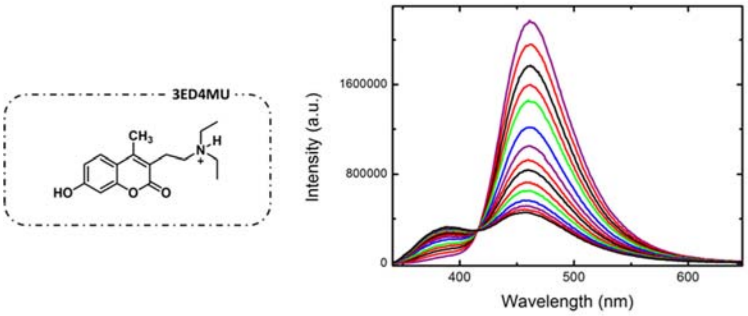
Coumarins are oxygen-containing molecules with specific benzopyrone nucleus. Different coumarins have been identified as antineurodegeneratives, anticoagulants, antioxidants, antimicrobials, anticancer, etc., compounds. [1] However, together with the effect of the drug, one important issue that has received less attention regards its delivery into the molecular target. Partial or full encapsulation within cucurbit[n]urils provides steric hindrance to drug degradation by peptides and proteins, and the use of different sized cucurbit[n]urils allows for the tuning of drug release rates, cytotoxicity and toxicity. [2] Moreover, there are some studies about the improvement of anticancer drug delivery using cucurbit[n]urils, and the transport of the CB host-guest supramolecular entities across the cell membrane. [3,4]



Scheme 1- Chemical structure of the studied ligand and steady-state fluorescence spectra of 3ED4MU upon the addition of increasing amounts of CB7 at pH = 3.

In this study we report a comprehensive photophysical and NMR investigation of the supramolecular encapsulation of an umbelliferone derivative (3ED4MU) with CB7. Steady-state, time-resolved fluorescence, ^{1}H NMR spectroscopy among others were used and a stoichiometric 1:1 CB7:3ED4MU complex was found in aqueous solution at pH 3.

Acknowledgements:
We acknowledge funding by FEDER (Fundo Europeu de Desenvolvimento Regional) through COMPETE (Programa Operacional Factores de Competitividade). The Coimbra Chemistry Centre is supported by the Fundação para a Ciência e a Tecnologia (FCT), Portuguese Agency for Scientific Research, through the programme UID/QUI/UI0313/2013. EDP acknowledges MATIS Project - Materiais e Tecnologias Sustentáveis, CENTRO-01-0145-FEDER-000014 for a post-doctoral grant.

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RED-ORANGE EMISSION IN Y_3TaO_7 SOLID SOLUTION CONTAINING HIGH Eu^{3+} CONCENTRATION FOR PHOTONICS APPLICATIONS

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Inorganic materials have been extensively used as rare earth (RE) ion hosts, due to their several properties that enable their large-scale application in photonics, such as optical amplifiers, LEDs, solar cells, lasers, phosphors and biomarkers [1]. Besides, Eu^{3+} ions are used as structural probe since their luminescence features strongly depend on the chemical environment. In this work, it is reported the synthesis, structural and spectroscopic characterization of Y_3TaO_7 containing high Eu^{3+} ions concentration prepared through an alternative route. Eu^{3+} solubility into Y_3TaO_7 was investigated, and how the incorporation of high Eu^{3+} concentration (from 7 up to 50 mol %) affects host stabilization and their luminescence features. Y_3TaO_7 solid solutions containing Eu^{3+} were prepared by the sol gel method using a controlled hydrolysis and condensation reactions of tantalum ethoxyde and $Y(NO_3)_3$ precursors in a basic and ethanolic solution. Solid products were annealed at 900 or 1100 °C for 2 h. Stabilization of Y_3TaO_7 orthorhombic crystalline phase, with space group *Ccmm*, was observed by X-ray diffraction as Eu^{3+} concentration increases, forming a substitutional homogeneous solid solution. In addition to the Y_3TaO_7 crystalline phase, a beginning of M'-$YTaO_4$ phase crystallization, with space group *P12/a1*, was evidenced for the samples annealed at 1100 °C by FT-Raman. Vibrational spectroscopies showed that both crystalline phases have relatively low energy corresponding to Ta-O and Y-O vibrational modes and an absence of OH and CH groups. The emission spectra have shown an intense broad band emission corresponding to the intraconfigurational $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) transitions, which indicates Eu^{3+} ions distribution in different symmetry sites into the Y_3TaO_7 solid solution. Luminescence spectra profile changes to sharper and more defined Stark levels when a small amount of $YTaO_4$ secondary phase is present, which indicate the preferential Eu^{3+} occupation in the symmetry sites of the $YTaO_4$ phase. A $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transitions intensity ratio values of about 3.3 and 2.2 were measured for the samples annealed at 900 and 1100 °C, respectively, indicating occupation of Eu^{3+} ions into relatively low symmetry sites. The intensity ratio values do not change significantly due to the occupation in the same average symmetry sites, even for the different spectral profile. The decay curves from the $^5D_0$ excited state have shown an almost single exponential profile, with minimum non-radiative processes due to RE concentration up to 20 mol% Eu^{3+} ions. $^5D_0$ excited state lifetime and quantum efficiency decreases only at highest Eu^{3+} concentration (more than 30 mol %) employed herein. Rising Eu^{3+} concentrations elicit negligible Eu^{3+} emission quenching, which makes them interesting compounds as high-intensity emitters in photonics. Besides, by changing their crystalline structure, emission color tunability from red to orange is resulted, which can be tailored by controlling the Eu^{3+} concentration into yttrium tantalate.

Acknowledgements

This work was supported by CNPq, CAPES and FAPESP (grant number 2018/04587-0). Funding was also provided by Fundação para a Ciência e a Tecnologia (FCT), EU/FEDER COMPETE within the scope of the projects CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013).

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PRODUCTION OF HYDROGEN AND BENZALDEHYDE: PHOTOCATALYTIC REFORMING OF BENZYL ALCOHOL OVER METAL-LOADED g-C_3N_4

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Hydrogen is an attractive form of energy both from the environmental and economic points of view [1]. One route towards the production of hydrogen is the photocatalytic reforming of organic compounds using semiconductor materials generating hydrogen and value-added chemicals under mild conditions of temperature and pressure [2].

In the present work, several g-C_3N_4 based photocatalysts [3] were synthetized and applied to the photocatalytic reforming of benzyl alcohol (BA) into benzaldehyde (BAL) and hydrogen. The main targets of this study were to study the influence of a thermal treatment to g-C_3N_4 and the deposition of different metals (Au, Pd, Pt and Ru) on the surface of the material.The photocatalytic experiments were carried out in a glass reactor, using a four LED system (λ_{max} = 417 nm) as irradiation source.

The occurrence of defects in the parent material and its influence on photocatalytic activity was investigated by photoluminescence and electron microscopy. The deposition of a metal over the g-C_3N_4 enhanced the efficiency of the materials. Among all the photocatalyst, Pt-loaded materials were the most efficient for the production of hydrogen, while Au was the best performing co-catalyst for the selective production of BAL (Fig. 1).

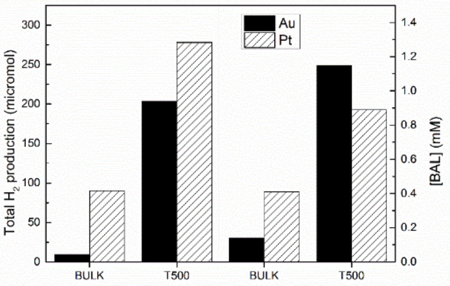

Figure 1. Total H_2 production and BAL concentration at 4h of irradiation, using g-C_3N_4 bulk and T500 with Au and Pt deposited.

The performance of g-C_3N_4 has explained in terms of a more pronounced separation of the layers of the material, resulting in a higher surface area. The photocatalytic performance of the metal-containing materials could be related to their dispersion over the carbon phase.

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TUNING THE TWO-PHOTON ABSORPTION PROPERTIES IN NANOGRAPHENE MOLECULES

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Graphene quantum dots (GQDs) have been extensively investigated in recent years due to their exceptional optical properties that enabled applications in bioimaging, sensors, optoelectronic devices and nanomedicine. However, due to their uncontrolled synthetic procedures the final material is quite heterogeneous making it impossible to control its properties and engineering the material for specific applications.[1]

To overcome this limitation, we initiated the study of the photophysical properties of well-defined nanographenes containing heptagonal carbocycles mimicking the structure of GQD. The step-by-step controlled synthetic procedure of these molecules leads to a homogenous material with well-defined molecular structure.[2] The presence of seven-membered rings induces a saddle-shape curvature in the planar network pushing the structure out of the plane affecting significantly their linear and nonlinear properties. For a set of nanographene molecules, the effect of the nature of the edge groups, the distortion from planarity and the conjugation length on the photophysical properties were studied, with emphasis on the two-photon absorption and emission. Theoretical calculations were performed to help in the understanding of the electronic transitions involved in the one- and two-photon absorption.

Figure 1 illustrates the one- and two-photon absorption spectra and the theoretical electronic transitions allowed for two nanographene molecules with different planarity.

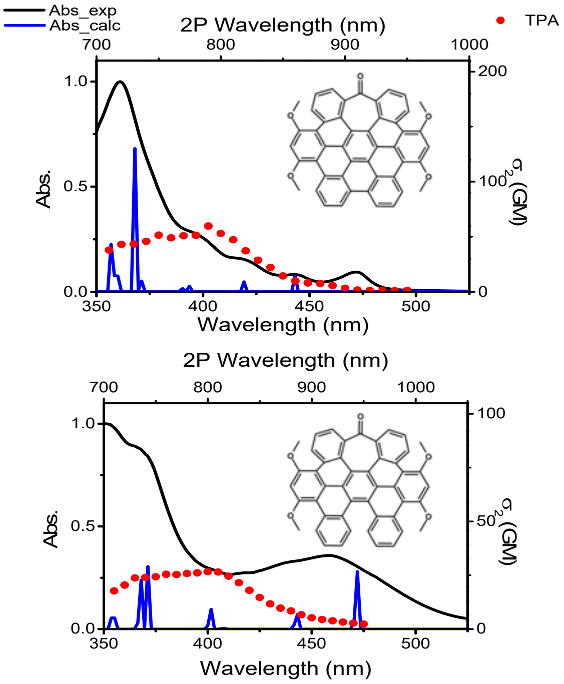

Figure 1: Experimental and calculated One-photon absorption (OPA) and experimental Two-photon absorption (TPA) for the respective molecule.

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STEREOCHEMICAL AND STERIC CONTROL OF THE OPTICAL SIGNATURES OF BICHROMOPHORIC DYES

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One of the hottest research topic nowadays in dye chemistry deals with the design of multichromophoric organic architectures. In demand to such concern, the famous BODIPY (boron dipyrromethenes) luminophores, in terms of modulable photonic behavior and rich chemical versatility,[1] are being the subject of many ongoing smart designs to develop multichromophoric systems. Among the most tested approaches, the covalent linkage of two identical chromophores (bis-BODIPYs) is deserving much attention. In these assemblies the spacer plays a key role in the final photophysical signatures of the resulting complex dye. Herein, we report a bis-BODIPY featuring rigid and compact BODIPY cores covalently linked through a tartaric acid at the chromophoric boron bridges (Figure 1).[2] The stereoisomeric properties of such tartaric spacer triggers the viability of intramolecular excitonic coupling, which determine the fluorescent and laser response of the dyad, as well as the optical activity. Thus, the achiral *meso* isomer (*R*,*S*) provides a fluorophore with high absorption and efficient laser output since both chromophoric subunits are electronically decoupled. However, the enantiomer (*R*,*R*) induces J-like like intramolecular excitonic coupling, as revealed by computational simulations (the overlap of the side pyrroles enables a head to tail interaction), and endowes with a chiral response against circularly polarized light to the whole dyad. Therefore, we are able to finely modulate the photophysical, lasing and chiroptical properties of bis-BODIPYs just choosing the suitable stereoisomeric form of the spacer (enantiomer or diastereoisomer). Moreover, the sole alkylation of the conformationally restricted chromophoric core adds a second level of control since it controls the magnitude of the exciton coupling (interchromophoric distance and relative orientation) and hence the fluorescent response of the intramolecular J-aggregate.

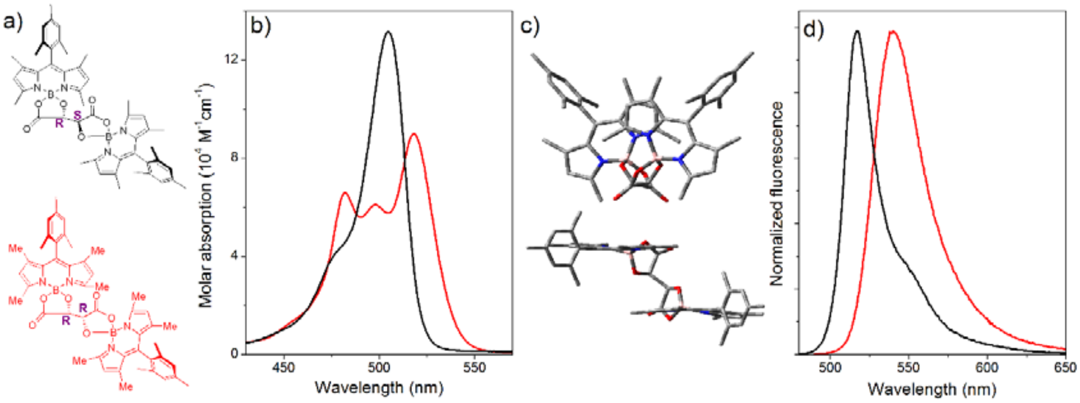

Figure 1. Molecular structure of representative bis-BODIPYs, identifying the chirality of the spacer (a). Absorption (b) and fluorescence (d) spectra of bis-BODIPYs bearing achiral (in black) and chiral (in red) tartaric. Optimized ground state geometry (wb97xd/6-311g**) of the last dyad (c) in two different views to emphasize the ongoing intramolecular J-like exciton coupling.

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SYNTHESIS OF AROMATIC ALDEHYDES USING A g-C_3N_4 PHOTOCATALYST

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The traditional methods adopted in organic synthesis and fine chemical industry generally involve the use of strong oxidants or reductants and the presence of metal catalysts increasing the cost and hazardousness of the process. The advantages of heterogeneous photocatalysis as alternative synthetic route includes the use of mild reaction conditions of temperature and pressure, with the use of water as solvent.

Graphitic carbon nitride (g-C_3N_4) a recent optical photocatalyst is gaining importance, due to this narrow band gap energy (2.7 eV), easy and relative low-cost preparation, and thermal and chemical stability [1,2], compared to the metal oxide semiconductors, such as TiO_2. In this work, g-C_3N_4 was synthesized by thermal decomposition of dicyandiamide followed by a thermal post-treatment at 500 ºC, as described elsewhere [1].

We performed the photocatalytic oxidation of different parent alcohols, namely anisyl, benzyl, 4-methylbenzyl, vanillyl and piperonyl alcohols, selectively into the corresponding aldehydes: anysaldehyde (AAD), benzaldehyde (BAD), tolualdehyde (TAD), vanillin (VAD) and piperonal (PAD). The initial concentration of the aromatic alcohols was 1.5 mM and the catalyst load fixed at 1 g L^{-1}. The suspensions were continuously stirred and saturated with air. As functional and versatile light sources we used UV-LEDs in order to take advantage of their high energy efficiency, life expectancy, low cost and process design flexibility.

Although the g-C_3N_4 material is very efficient for the synthesis of AAD, TAD and BAD (Fig. 1), its shows a negligible activity for the synthesis of PAD and VAD. The distinct behaviours observed for the synthesis of the different aldehydes can be rationalized in terms of the molecular structure of the different precursor molecules, considering the number of substituent groups, their electronic nature and position in the aromatic ring.

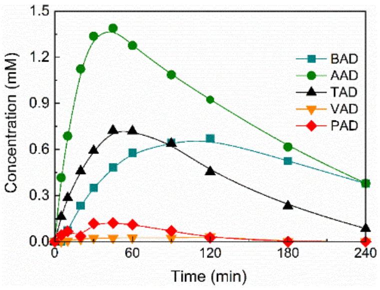

Figure 1. Concentration profiles of aromatic aldehydes during the photocatalytic synthesis using g-C_3N_4.

Acknowledgements: This work is a result of project ''AlProcMat@N2020 – Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020'' (NORTE-01-0145- FEDER-000006), supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C.G.S. acknowledge the FCT Investigator Programme (IF/00514/2014) with financing from the European Social Fund (ESF) and the Human Potential Operational Programme. R.A.F. acknowledges the PhD fellowship funded by Project NORTE-08-5369-FSE-000028, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the ESF.

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AGGREGATION-INDUCED EMISSION VS. AGGREGATION-CAUSED QUENCHING IN TETRAPHENYLETHENE-SUBSTITUTED POLYTHIOPHENES

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Polythiophenes are amongst the most studied conjugated polymers due to their applications in the last generation of optoelectronic devices, namely in organic solar cells light-emitting diodes and field effect transistors.[1] However, an obstacle to their development is the significant fluorescence quenching in the solid state that generally occurs due to strong interchain interaction of the polythiophenes. This phenomenon can be referred to as aggregation-caused quenching (ACQ). This may dramatically affect the performance of the polymers for optoelectronics because for practical applications they are commonly used as solid films . Several chemical, physical and engineering strategies have been developed to overcome the ACQ effect by, for example, attachment of bulky alicyclics, encapsulation by amphiphilic surfactants, and blending with transparent polymers.[2] These processes, however, are often accompanied by severe side effects. For example, the steric effects of bulky alicyclics, can twist the conformations of the chromophoric units and hinder the electronic conjugation on the polymers, while the electronic effects of the saturated surfactants and non-conjugated polymers can dilute the chromophoric units densities and block the charge transport in electroluminescence (EL) devices. In this work an attempt was made to circumvent the ACQ effect by synthetizing tetraphenylethene (TPE)-substituted polythiophenes. The TPE molecule with their propeller shaped conformation has been in the forefront of the development of the concept of aggregation induced emission (AIE) in which molecules displaying very weak fluorescence in dilute solutions (in good solvents) become highly emissive upon aggregation in poor solvents or cast into solid films. Indeed, it has been demonstrated that TPE with its propeller-shaped conformation is an AIE active chromophore.[3] It was demonstrated that the AIE effect is caused by the restriction to intramolecular rotations (RIR) in the AIE active molecules by the aggregate formation, which effectively blocks the non-radiative energy dissipation channels and favors the radiative decay. With aggregates, the propeller-shaped TPE units prevent the molecules from packing in a π–π stacking process, while their intramolecular rotations are physically constrained in the solid state. The comprehensive spectroscopic and photophysical study of two polythiophenes comprising tetraphenylethene-substituted thiophene (homoPT) and -bithiophene (coPT) building blocks was carried out in solution and in the solid state (thin films). In addition, for comparison purposes the investigation of the parent poly(3-hexylthiophene), displaying a similar degree of polymerization, together with the monomeric percursor tetraphenylethene-thiophene was performed. From the data collected in the solid state and THF:water mixtures (where aggregation is induced) it was found that for the homoPT and P3HT polymers aggregates the ACQ effect is predominant, while in the case of the coPT polymer the two mechanisms (ACQ and AIE) are operative.

Acknowledgments

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PHOTOLUMINESCENCE PROPERTIES OF LANTHANIDE COMPLEX: UREASILS VERSUS POLY(METHYL METHACRYLATE)

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Europium complex with trifluoroacetylacetone ($Eu(tfac)_3 \cdot H_2O$, tfac=trifluoroacetylacetone) was doped into different matrices, di-ureasil (d-U(600)), tri-ureasil (t-U(5000)) and poly(methyl methacrylate) (PMMA) and the resulting hybrids were characterized by XRD, FT-IR, ^{29}Si NMR, and photoluminescence spectroscopy. The results show that compared to the pure $Eu(tfac)_3 \cdot H_2O$ powder, the hybrids based on the ureasils (d-U(600) and t-U(5000)) display higher quantum yields, whereas the hybrid obtained from PMMA exhibits a similar quantum yield, which can be rationalized by the coordination environments of the complexes in the hybrids.

EFFECTS OF CONJUGATION EXTENT OF OLIGOPERYLENES ON THEIR SPECTROSCOPIC PROPERTIES.

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We synthesized a series of new oligoperylenes with varying conjugation length to investigate the effect of conjugation on their spectroscopic properties, using as the reference compound, perylene (**P**). The oligomers have two (**P_2** and **P_2T**) or three (**P_3T**) perylene units alternating with simple bond (**P_2**) and triple bonds (**P_2T** and **P_3T**). The structures of the compounds studied are shown in **Figure 1**. Electronic properties were investigated using the density functional theory (DFT) methods.

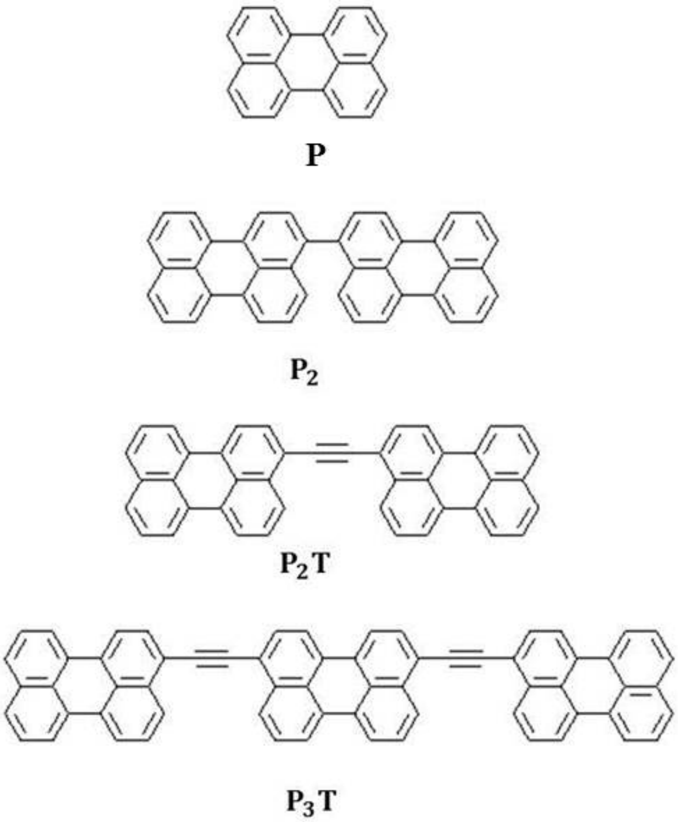

Figure 1. Chemical structures of the compounds.

IN VITRO ASSAYS OF INFRARED TO VISIBLE UPCONVERSION NANOCRYSTALLINE Y_2O_3: Er^{3+}/Yb^{3+} NANOPARTICLES FOR THERANOSTICS.

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In the last few years, the application of luminescent lanthanide doped nanoparticles has played a fundamental role as fluorescent nano probes for *in vivo* and *in vitro* imaging [1] besides their use as energy converters to induce a photochemical process in biological medium. This multifunctionality makes them interesting plataforms for theranostics. In this way, Er^{3+} and Yb^{3+} co-doped materials can exhibit an interesting near infrared to visible (green and red emission) upconversion process, which makes them promising for biological applications for bioimaging combined to photodynamic therapy. Furthermore, the intensities of their emissions can be used to determine de local temperature [2]. In this context, Yttrium Oxide has been extensively studied as rare earth host due to low phonon energy, high lanthanide solubility and low toxicity. In this work, we report the synthesis and luminescence properties of Er^{3+}/Yb^{3+} co-doped Y_2O_3 nanoparticles and in vitro assays with brain glioblastom cells T98G and U87MG. The nanoparticles were synthesized by an homogeneous precipitation method: firstly Er^{3+}/Yb^{3+} co-doped $Y(OH)CO_3$ nanoparticles were prepared using $Y(NO_3)_3$, $Er(NO_3)_3$ and $Yb(NO_3)_3$ solutions as precursors and urea decomposition. The $Y(OH)CO_3.nH_2O$ nanoparticles were annealed for 2 hours at 900° C yielding Y_2O_3 formation. Structural, morphological, spectroscopic measurements were performed by X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrational spectroscopy – FTIR, and photoluminescence. The cell viability was performed by colorimetric test MTT with brain glioblastom cells T98G and U87MG. Spherical and mono dispersed polycrystalline particles, with a narrow size distribution around 100 nm, were observed by TEM analysis. The colloidal stability of particles in suspension was confirmed by zeta potential and dynamic light scattering. Cubic crystalline phase of Y_2O_3 was identified by comparison with the XRD patterns. In the FTIR spectrum was noticed strong peaks at 560 cm^{-1}, 465 cm^{-1} and 436 cm^{-1} ascribed to the stretching vibrational modes of the Y-O. Low intensity peaks at 3500 cm^{-1} and 1500 – 1400 cm^{-1} are assigned to hydroxyl and carbonate groups respectively, indicating a low residual content. Upconversion photoluminescence in the visible region were observed even at aqueous medium. The Er^{3+} emission exhibited band at 18570 cm^{-1}, 17740 cm^{-1} and 15120 cm^{-1} assigned to $^2H_{11/2} \rightarrow 4I_{15/2}$, $^2S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$. The colorimetric test MTT showed the highest cell viability for Y_2O_3 concentrations of 1,3 mg/mL and 1,7 mg/mL at cell medium for T98G cells. Based on these studies, Er^{3+}/Yb^{3+} co-doped Y_2O_3 nanoparticles are promising materials for biological application, specifically bioimaging and photodynamic therapy using as an excitation source near infrared radiation.

Acknowledgements

The authors are grateful to FAPESP, CAPES, CNPq and PRONON for financial support. Funding was also provided by Fundação para a Ciência e a Tecnologia (FCT), EU/FEDER COMPETE within the scope of the projects CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013).

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NEW ACRIDONE POLARITY PROBES FOR FLIM IMAGING

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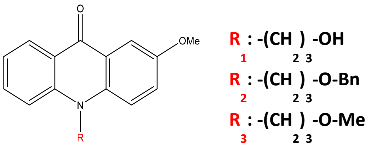
Acridones are heteroaromatic compounds with long fluorescence lifetimes (>10 ns) and good quantum yields (>0.5), exhibiting emission wavelengths in the blue region 400-500 nm. They have been employed in several applications such as DNA sequencing, monitoring of enzymatic systems, detection of biomolecules, intracellular sensing (Ca^{2+}, Cu^{2+}, H^{+}…), and as antitumoral drugs [1].

In this study, we explore the influence of solvent polarity and pH on the photophysical and photochemical properties of newly designed acridone derivatives. These compounds were synthetized with 3 different substituents in the nitrogen position in order to tune their fluorescent properties (Scheme 1). Absorption and emission spectra, quantum yields and fluorescence lifetimes have been obtained in different solvents and in aqueous solutions. Our results show great dependence of their with polarity, resulting in bathochromic shifts for absorption and emission spectra and a significant increase in their fluorescence lifetimes.



Scheme 1.- Chemical structure of the acridon developed in this work

The three different substituents cause slight effects on the fluorescent (Figure 1), pointing out an excellent strategy to functionalize these fluorophores with other interesting sensing reporters. These excellent properties specially the particularly long fluorescence lifetimes, make these acridones promising candidates as FLIM probes [2].

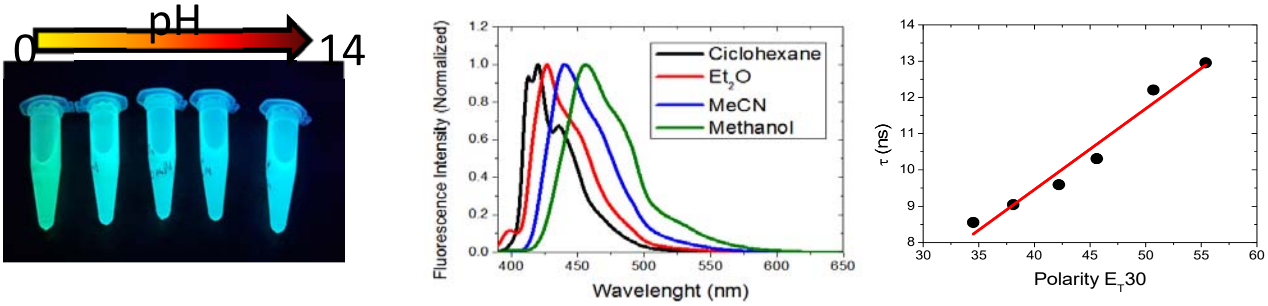


Figure 1.- Changes in acridone's properties dissolved in different solvents .

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DIKETOPYRROLOPYRROLE- PERYLENEDIIMIDE COMPOUNDS AS LIGHT HARVESTING SYSTEMS AND AS NON-FULLERENE ACCEPTORS IN ORGANIC SOLAR CELLS

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Increased energy consumption, contamination and the scarcity of fossil resources have led to the development of cleaner and sustainable new alternative energy sources that met the needs of today's society. Solar cells based on organic materials have been studied due to their low cost, sustainable capacity and structural flexible. [1,2] Organic Solar Cells (OSCs) need active materials to perform specific functions like light absorption, charge separation and charge transport. [3] Light harvesting systems in OSCs require the presence of two types of subunits, an electron-acceptor and an electron-donor. [4]

In this context, we decided to synthesize a series of compounds with diketopyrrolopyrrole (DPP) donor units, coupled with perylenediimide (PDI) acceptor groups. DPPs are well known for their good charge mobility, chemical versatility and high stability.[5-7] On the other hand, PDIs are also a type of compounds with an attractive interest due to its high thermal, chemical and photochemical stabilities.[8-10]

In the present work, we will present the synthesis, characterization and the photophysical properties of DPP-PDI derivatives as the represented in Figure 1.

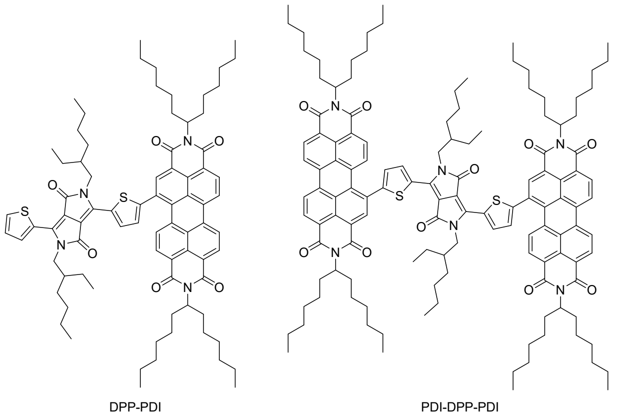

Figure 2- Structure of DPP-PDI and PDI-DPP-PDI, respectively.

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LUMINESCENT IONOGELS INCORPORATED INTO PMMA

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Trivalent lanthanide-based (e.g., Eu^{3+}) complexes usually exhibit attractive photoluminescence features, but poor mechanical properties and low thermal stability. These drawbacks can be overcome by combining lanthanide-based complexes with ionic liquids (ILs),described as molten salts with melting point below 100 ºC, with a myriad of attractive properties, such as high thermal stability, low volatility, high ionic conductivity and wide electrochemical stability window. The combination of these two types of materials can result in a luminescent ionogel system, which can be described as a multifunctional material encompassing high ionic conductivity, high thermal stability, good mechanical properties, wide electrochemical stability, high quantum efficiency.[1] Poly(methyl methacrylate) (PMMA) is a very well known, low-cost, environmentally friendly and harmless polymer with exceptional optical properties.[2] It is one of the most popular polymer-based host matrixes for luminescent lanthanide-based complexes[1] and one among the promising representatives of polymeric materials with large application in optoelectronic devices.[3] In previous works, PMMA has demonstrated excellent results and compatibility with different lanthanide-based complexes and ILs.[1] Luminescent polymeric-based films can maintain or even boost the luminescent properties of the complexes, and can be easily processed into films for example by solvent casting yielding materials which are mechanically more flexible than previous polymeric-based host matrixes incorporation.[4] Consequently, the resulting materials are very interesting for applications in photovoltaic (PV) cells, and luminescent electrochromic devices (ECDs) with uninterrupted near-infrared (NIR) light transmission. In the present study, ionogels composed of a sol-gel-derived silica network containing pendant chains with an imidazolium cation end group and a lanthanide (Eu^{3+}, Tb^{3+}, Nd^{3+} and Yb^{3+})-based complex anion were synthesized. Detailed investigations were performed using ATR-FTIR, TGA, DSC, SEM, TEM, XRD, POM, contact angle measurements and photoluminescence spectroscopy. The matrix effect on the properties of the lanthanide-based ionogels was also studied and the concentration effect was addressed.

This work was supported by National Funds by FCT - Foundation for Science and Technology (PTDC/CTM-NAN/0956/2014), FEDER funds through the POCI - COMPETE 2020 - Operational Programme Competitiveness and Internationalization in Axis I - Strengthening research, technological development and innovation (POCI-01-0145-FEDER-007491 and Pest-OE/QUI/UI0616/2014), the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Marita A. Cardoso thanks FCT for grant SFRH/BD/118466/2016.

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THE DEVELOPMENT OF A NEW SUNSCREEN-BASED PHOTOCAGED SYSTEM. ITS APPLICATION IN A KETOPROFEN-OXYBENZONE DYAD.

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This work focuses the attention on the development of a new photoprotection strategy in order to counteract the photosensitizing effects of some drugs on biomolecules[1]. Among the photosensitizing substances, nonsteroidal anti-inflammatory drugs (NSAIDs) for topical use are particularly important due to their extensive use in daily life, especially by outdoor workers or sportsmen. The most representative example of this family is ketoprofen (KP), a drug that is responsible for pronounced cutaneous photosensitization[2]. That is the reason why ketoprofen has been chosen for the present work.

In this research, we have developed a new sunscreen-based photocaged system. Such system is able to photorelease both KP and a solar filter, oxybenzone (OB), which should prevents the harmful drug effects caused by UVB and UVA radiation.

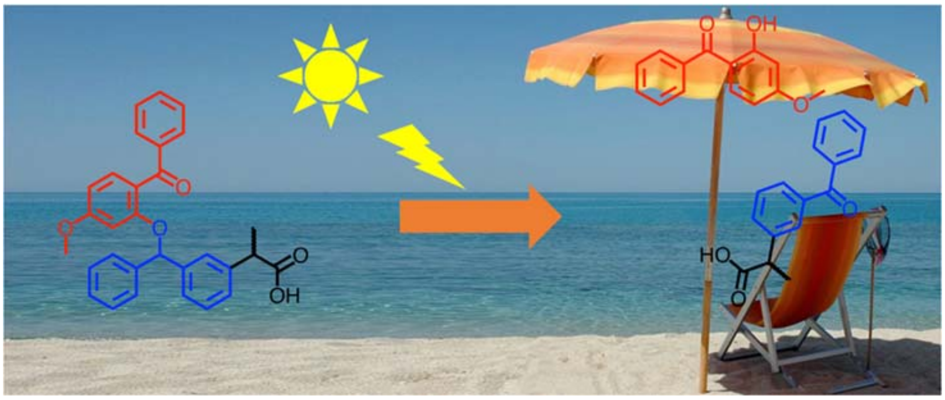

Figure. Structure of the dyad oxybenzone-ketoprofen and the photorelease of its components.

As a first step, since ketoprofen is a benzophenone derivative, a model oxybenzone-benzophenone system (OB-BP) was prepared to evaluate the photorelease of both the oxybenzone filter and the benzophenone moiety. The photophysical properties of the dyad were investigated using UV-Vis absorption, phosphorescence emission and laser flash photolysis. Photorelease experiments were carried out in polar protic and aprotic solutions, and were followed by means of a HPLC coupled to a diode array detector as well as by means of an UPLC coupled to a mass spectrometer. In these studies, it was observed the photorelease of the benzophenone and the oxybenzone in different yields.

Finally, as a real application of the model, the dyad oxybenzone-ketoprofen (OB-KP) was prepared. Photorelease experiments were also carried out in different solvents and they were assessed by UPLC coupled to a mass spectrometer. From these studies, it was observed that ketoprofen is effectively photoreleased.

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ASSESSING LI$^+$ ROLE IN EMISSION ENHANCEMENT OF (YYBER)$_2$O$_3$ UPCONVERTING NANOPARTICLES

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Over the past few years, the ability of trivalent lanthanide (Ln^{3+})-doped nanocrystals to convert near-infrared light into tunable visible emission (photon upconversion) has received much attention and led to important emerging applications, e.g., single-particle tracking, bio-imaging and therapeutics, thermal sensing, photovoltaics, anti-counterfeiting, and full-color volumetric 3D display.[1-3] However, due to the parity forbidden character of the intra-4f Ln^{3+} transitions and the nonlinear optical processes in upconversion, the emission intensity is in general too low to fulfil the growing demand for developing efficient light emitting materials. As such, among the various promising strategies used to enhance the upconversion emission of Ln^{3+}-doped nanocrystals, including surface coating and core-shell structuring, changing the Ln^{3+}concentration, plasmonic coupling, and co-doping with alkaline ions, that induced by Li$^+$ doping has been contentious, qualitative, speculative and poorly understood.

In this work, we report the first quantitative assessment of Li$^+$-induced upconversion enhancement based on the measurement of the absolute emission quantum yields and using $(Y_{0.97-x}Yb_{0.02}Er_{0.01}Li_x)_2O_3$ nanocrystals, x=0.000–0.123, as a model system.[4] Co-precipitation and solid-state reaction synthesis methods are appraised for their ability to effectively dope the nanocrystals with Li$^+$. In contrast with numerous reports, elemental analysis revealed that the co-precipitation synthesis procedure yielded no Li$^+$ in the final upconverting nanocrystals. The solid-state reaction route accomplished an effective Li$^+$ doping and the emission quantum yield increased tenfold with increasing Li$^+$ content up to x=0.123, reaching a maximal value of 0.04% at x=0.031. Moreover, we show that the unit cell parameter of the host lattice and the crystallite size are the prime sources of the quantum yield enhancement and, then, of the upconversion emission boosting.

Acknowledgements

This work was partially developed in the scope of the project CICECO-Aveiro Institute of Materials (Ref. No. FCT UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. Financial support of Fundação para a Ciência e a Tecnologia (FCT) under projects PTDC/CTMNAN/4647/2014, POCI-01-0145-FEDER-016687 and POCI-01-0145-FEDER-031469 is acknowledged. MLD thanks FCT for the post-doctoral grant (SFRH/BPD/93884/2013).

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LNATHANIDE COMPLEXES FUNCTIONED DI-UREASILS BY IN-SITU SOL-GEL SYNTHESIS

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Herein, in order to investigate the near-UV induced white materials for light light, organic–inorganic di-ureasil hybrid (d-U(600)) functioned with 4,4-oxybis(benzoic acid) (Oba) and 1,10-phenanthroline (Phen) as ligands of lanthanide complexes were fabricated by in-situ sol–gel process. X-ray diffraction, Fourier transform infrared, ^{29}Si magic-angle spinning (MAS) and ^{13}C cross-polarization MAS nuclear magnetic resonance spectra, and thermogravimetric analyses were introduced to investigate the structure stabilities after doping. Meanwhile, PL excitation and emission spectra at room temperature and low temperature were discussed to understand ions local shell coordination situations. Furthermore, the UV–Vis, low temperature measurement of di-ureasil hybrid embeded Gd complex and intensity decay cuves were used to analyze the energy transfer mechanisms. The results show that these Ln^{3+} complex based di-ureasils exhibit promising luminescent features, e.g. 39.0±3.9% of quantum yield of 6Eu(Oba)$_{1.5}$(Phen)$_{1.5}$@dU6 under λ_{ex}=295 nm irradiation. The energy levels and energy transfer mechanism figured out that Eu^{3+} emission through a two-step intermolecular energy transfer process, namely, between (i) T$_1$ of Oba to T$_1$ of Phen followed by T$_1$ of Phen-to-Eu^{3+} energy transfer, and (ii) between T$_1$ of Oba and hybrid, followed by hybrid-to-T$_1$ of Phen-to-Eu^{3+} and hybrid-to-Eu^{3+} energy transfer, as well as no energy transfer between the Ln^{3+} ions. Based on above studies, a triple-doped di-ureasil, 3Gd$_{0.91}$Eu$_{0.05}$Tb$_{0.04}$(Oba)$_{1.5}$(Phen)$_{1.5}$@dU6, was prepared and it can give very pure white light emission at 310 nm irradiation with CIE coordinate of (0.33, 0.35) very closing ideal (0.33, 0.33) white light.

STUDY OF INTRINSIC DNA DAMAGE THE ETHENO DERIVATIVE.

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The study of the DNA chemical modifications has been boosted during the last decades due to the importance of DNA damages in the development of skin cancer.
In spite that DNA barely absorbs UVA, which is the most important part of the UV radiation reaching the Earth surface, damages can occur by photosensitization through the action of exogenous or endogenous compounds.

In this context, recent investigations have indicated that (6–4) photoproducts, resulting from direct irradiation of DNA, may act as effective endogenous photosensitizers, as their 5-methyl-2-pyrimidone substructure mediates the photoinduced generation of cyclobutane pyrimidine dimers and single strand breaks (ssb) in DNA. [1]

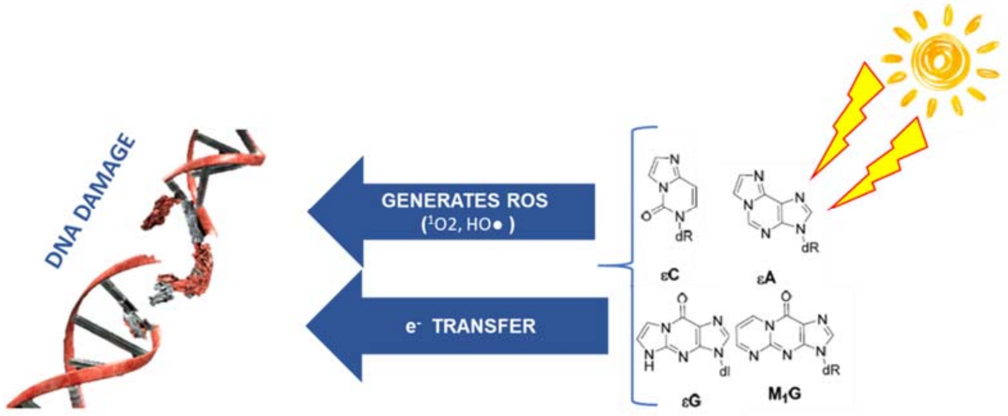

Figure 1. Explanation of possible clustered DNA damage process caused by lipid peroxidation derived DNA lesions.

In this work, DNA damages arising from lipid peroxidation are considered (Figure 1). These lesions present an interesting red shifted UV-Vis absorption by respect with the canonical DNA bases, which is due to their extended π-conjugation. Some of them, as εA, show an intense fluorescence emission in the visible region with a relatively long lifetime when excited at a lower energy than its canonical counterpart. Laser flash photolysis studies have also been carried out to gain more information on the generation of transient species that can affect the DNA integrity.

All these characteristics make these lesions good candidates to act as a Trojan horse, photosensitizing more damages in their neighbourhood.

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STUDY ON PHOTOPHYSICAL PROPERTIES AND ENERGY AND ELECTRON TRANSFER IN PORPHYRIN-PHTHALOCYANINE HETEROTRIMERS

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The key factors in photosynthesis include photoinduced energy and electron transfer in the photosystem with participation of chlorophylls and quinones.[1-3] Great efforts have been made to mimick these artificial photosystems, as photoconductors, organic semiconductors and energy harvesting photovoltaic devices, which are a few of their vast applications.[4,5] According to the structural similarity to the natural light harvesting chlorophyll material, a combination of porphyrins (Ps) and phthalocyanines (Pcs) macrocycles could act as chromophores with special and distinctive electronic properties. The role of Ps in natural photosynthetic systems has led to their extensive use as electron donors in biomimetic compounds,[6,7] while Pcs are involved in such systems due to their outstanding characters, *e.g.*, enhanced absorptive cross section at wavelengths corresponding to maxima of solar spectrum including near-IR, relatively easier oxidation, higher fluorescence quantum yield (6−10 times larger), and higher rigidity and photostability compared to Ps.[8,9] It is noteworthy that the Ps absorption bands lie in the visible region and the emission spectra of Pcs do not significantly overlap with those of Ps.[10]

In this work, we will present the synthesis and characterization of new porphyrin-phthalocyanine heterotrimers as the represented in Figure 1 and investigate their photophysical properties.

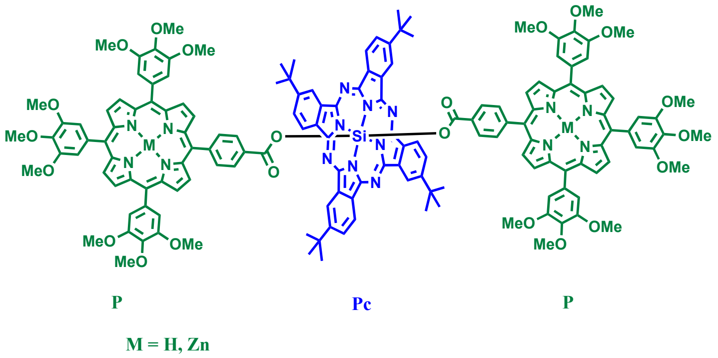

Figure 3. Structure of P-Si-Pc and its zinc complex.

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A TIME RESOLVED MECHANISTIC STUDY BASED ON METAL-FREE PHOTOCATALITIC REDUCTIVE DEHALOGENATION MEDIATED BY VISIBLE-LIGHT

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Visible-light mediated photocatalysis is a potential area with current interest in different fields such as development of new synthetic routes or pollutants treatment. Over this methodology reactions are able to run under mild conditions, therefore the interest over its performance is becoming an attractive field in the scientific community[1], even more if metal-free photocatalysts, such as dyes, are used. Riboflavine, RF (figure 1), a natural dye present in waters and which is responsible for the redox activity of cofactors flavin adenine dinucleotide (FAD) and flavin mononucleotide (FMN) presents a suitable redox potential that can be excited using safe visible light, therefore it can be used as a photocatalyst. In this context, a deep understanding of the mechanism behind the photocatalytic reactions attending to the kinetics of the excited states involved is always desirable. However, despite the growth of the area, the elucidation of the mechanisms involved is not easily assed due to the highly specialized equipment needed.[2]

Under this context, the aim of the present contribution is to study the reductive dehalogenation of different bromide derivatives, using visible light and RF in the presence of an amine as electron donor. Besides, a detailed mechanistic study, using fast kinetic tools, will allow to monitor the species involved in each step of the photoredox process. Therefore, an overall analysis of the mechanism will be undertaken including thermodynamic and kinetic data.

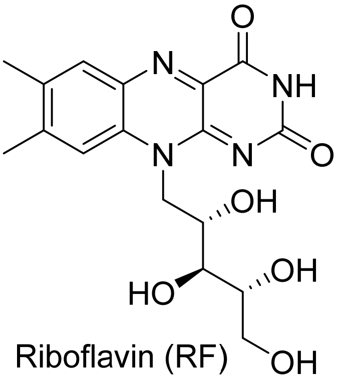

Figure 1: Chemical structure of RF

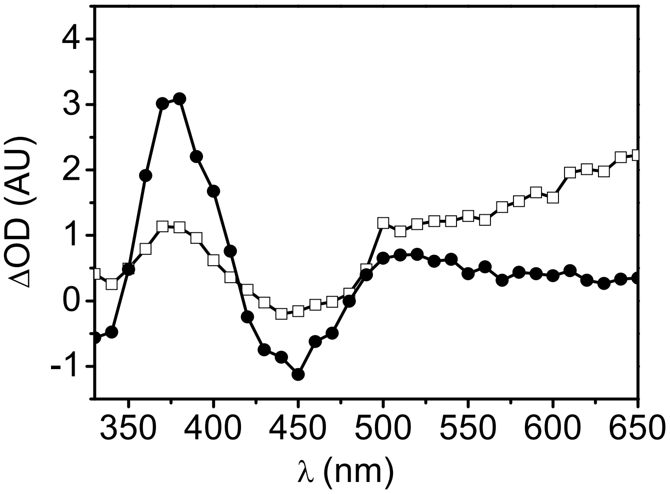

Figure 2: Transient absorption spectra of RF upon LFP excitation 2 μs after the laser pulse, in the absence (blank squares) and in the presence of 5.4×10^{-2} M DABCO (solid black circles).

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WATER SOLUBLE ELECTROLYTES FOR REDOX FLOW BATTERIES: A SPECTRAL, PHOTOPHYSICAL AND ELECTROCHEMICAL STUDY.

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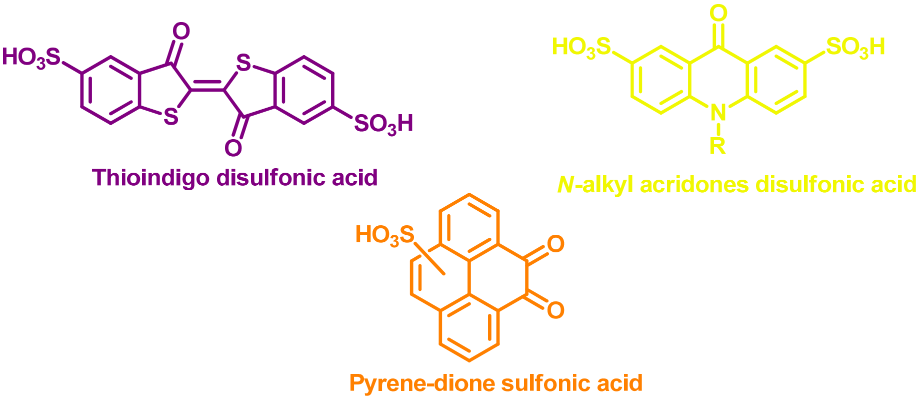
The global population growth impels the increase of energy consumption. It is thus mandatory to supplement the world needs in a sustainable way[1]. Redox Flow Batteries (**RFB**) are an emerging power source frequently described as affordable, reliable and ecofriendly depending on the used materials[2]. In our effort to synthesize new water soluble electrolytes for **RFB**, we were able to evaluate the applicability of different families of compounds namely, thioindigoids[3], acridones and polycyclic aromatic hydrocarbon diones (e.g. Pyrene-dione) derivatives. In this work, a comprehensive electronic spectral, photophysical and electrochemical investigation is presented for the three families of electrolytes. Additionally, with selected electrolytes a prototype of a **RFB** will be presented.



Scheme 1- Examples of the the investigated compounds.

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Acknowledgments

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This work was performed under the project “SunStorage - Harvesting and storage of solar energy”, with reference POCI-01-0145-FEDER-016387, funded by European Regional Development Fund (ERDF), through COMPETE 2020 - Operational Programme for Competitiveness and Internationalisation (OPCI), and by national funds, through FCT. RCP and ADRP acknowledge Sunstorage for respectively research and post-doctoral grants.

LUMINESCENT DOWNSHIFTING LAYERS BASED ON Eu^{3+}-DOPED ORGANIC-INORGANIC HYBRID MATERIALS FOR PHOTOVOLTAICS

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The mismatch between the AM1.5G spectrum and the photovoltaic (PV) cells absorption is one of the most limiting factors for their performance. Among the proposed strategies to overcome this issue luminescent downshifting (LDS) layers can be a very promising one.[1] LDS layers are coatings directly applied on the PV cell surface/bottom which absorb the incident radiation complementary to that of the PV cell which is then re-emitted at a specific wavelength that is refracted/reflected towards the PV cell.

Several studies showing improvements of solar cells using different luminescent downshifting materials, such as organic-dyes, quantum dots (QDs), and rare earth coordination complexes, mainly based on Eu^{3+} ions, have been reported.[1] In fact, Eu^{3+} complexes have many advantages due to their high luminescence and photostability being characterized by an emission profile centered at 615 nm matching the maximum spectral response of silicon (Si) based solar cells. Moreover, Eu^{3+} based complexes display significantly larger Stokes shifts compared to organic dyes or QDs, which minimizes self-absorption losses.[2]

In this work, we report the use of an organic-inorganic hybrid material, the di-ureasil d-U(600), doped with the $Eu(tta)_3{\cdot}2H_2O$ complex to be used as LDS layer in Si PV cells. The electrical measurements on the PV cell before and after the deposition of the LDS layer confirm the positive effect of the coating on the performance of the PV cell, with a relative increase on the maximum delivered power of ~9%. Also, the coated PV cell was used in a small solar car, which presented a relative increase in the velocity of ~9% when compared to the solar car with the bare PV cell.

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PHOTOPHYSICAL CHARACTERIZATION OF NEW ORGANIC MOLECULES WITH TADF

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Thermally activated delayed fluorescence (TADF) is an uncommon type of molecular fluorescence resulting from both singlet and triplet state properties: the emission spectrum is identical to that of normal (prompt) fluorescence, whereas the lifetime is close to that of phosphorescence [1]. Owing to the oxygen and temperature dependences, TADF can be used both in molecular thermometry and oxygen sensing [2]. In addition, TADF is at the heart of 3rd generation organic light-emitting diodes (OLEDs) [3,4]. To have an efficient TADF emission, several conditions are required. One of the most important requirements is a small value for the singlet-triplet energy gap (ΔE_{ST}). The design of new molecules for OLEDs has as one of the main goals a reduced ΔE_{ST} [5].

Herein, we use several methods of analysis to estimate the ΔE_{ST} of several molecules, designed by us. In addition, further important parameters such as the singlet and triplet formation quantum yield and the phosphorescence lifetime are also discussed.

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SMART POLYELECTROLYTE CAPSULES FROM PORPHYRINOID-GOLD HYBRIDS

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Polyelectrolyte microcapsules (PECs) are recognized systems for drug delivery. They can be easily prepared using layer-by-layer approaches under mild conditions and have unique properties such as large drug adsorption, controllable surface and stimuli responsiveness.[1] The incorporation of photodynamic and fluorescent molecules in these platforms imparts interesting therapeutic and imaging properties and opens a new gateway to cancer therapy and early diagnosis.

Owing to their preferential accumulation in cancer cells, high $^1O_2$ quantum yields and fluorescence, porphyrinoids have been extensively studied and some of them already approved for cancer therapy and imaging. One of the major drawbacks for porphyrin application in imaging is their low fluorescence quantum yield.

Gold nanoparticles (GNP) have unique optical properties that makes them very interesting for a range of applications. These particles strongly absorb and scatter light in the NIR region of the spectra. Fluorescence enhancement of weakly emitters is other point of active research with potential to improve image contrast for fluorescence-based bioimaging. [2]

In this work we have prepared a porphyrinoid–gold nanohybrid with significantly enhanced fluorescence due the plasmonic antenna effect of GNPs, through a rational design of polyelectrolyte core-shell-GNPs-porphyrinoid adsorbed in the same device.[1] Porphyrinoids and GNPs adsorption was followed by UV/Vis absorption and charge reversal from Zeta potential measurements. The emission enhancements were accompanied by shortening of fluorescence decay lifetimes, as viewed by fluorescence lifetime imaging microscopy (FLIM). Scanning electron microscopy (SEM) provided useful information about structure/topology of unmodified *vs* doped polyelectrolyte capsules. Fluorophores' lifetime and intensity distributions were also followed by FLIM.

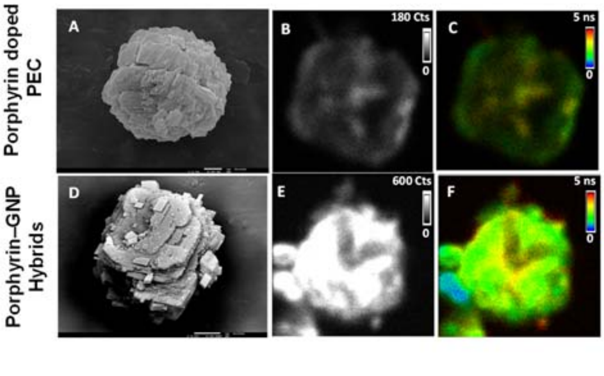

Figure. Porphyrin doped PECs and Porphyrin-GNP hybrids: (A,D) SEM (B,E) Fluorescence Intensity (C,D) FLIM.

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FLUORESCENT SILICA NANOPARTICLES: EFFECT OF SIZE AND FLUOROPHORE LABELLING DEGREE

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In the past decades fluorescence nanoparticle probes have successfully been exploited for bioimaging, biomarker and immunoassay applications. In particular, silica nanoparticles (SiNPs) present several advantages such as biocompatibility, large surface area and facile size control and functionalization. Dipyrromethene boron difluoride (BODIPY) dyes are known as efficient dyes due to their intense absorption and high fluorescence quantum yields. However, poor solubility in water limits their use. [1] Therefore, the goal of research was to covalently attach BODIPY to SiNP intended for use as biomarker.

SiNPs were synthesized by Stöber process and amino-functionalized by reaction with APTMS (figure 1 left). Fluorescent SiNPs were prepared by covalent attachment of BODIPY dye to the amino-modified surface of SiNPs. [2] The resulting particles were characterized in terms of size and zeta potential, using TEM (figure 1 right) and DLS. The size of nanoparticles was varied between 100 and 450 nm, and also the amount of BODIPY utilized in the reactions to study autoquenching of the fluorophore. Photophysical studies were performed by recording the emission spectra of the fluorescent SiNPs in ethanol and water (figure 1 center).

The obtained results indicate a size dependent degree of labelling, with the smallest particles (100 nm) yielding higher fluorescence intensities. Additionally, quenching of fluorescence in water was noted in all cases. DLS studies demonstrate this could be due to significant aggregation of nanoparticles in water. On the other hand, particles with higher degree of labelling exhibit an increase in polydispersity, as well as slightly more red-shifted emission spectra. For biological application, results point to the use of smaller particles which produce signals in aqueous media or a necessity for encapsulation of the dye inside the particles to protect it from the environment.

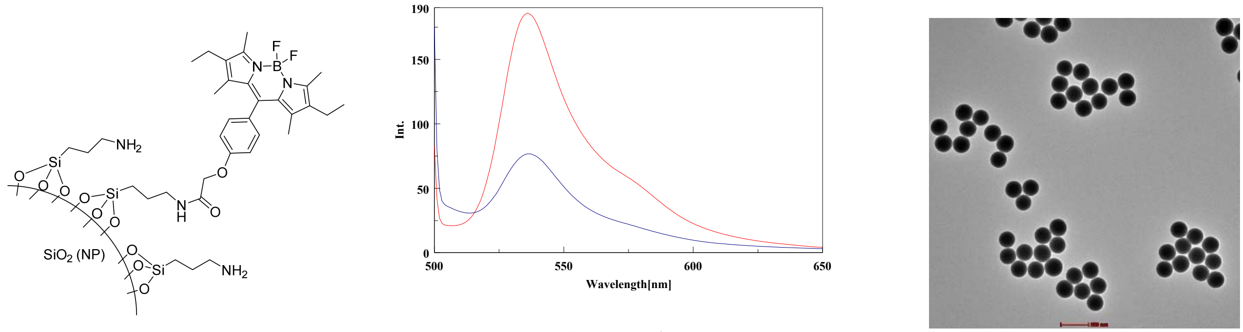

Figure 1

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