

Abstract Book

III Jornadas Ibéricas de Fotoquímica



**Granada,
4th-7th September, 2011**



PRESENTATION

ABSTRACT BOOK – III JORNADAS IBÉRICAS DE FOTOQUÍMICA
Edited by: Ángel Orte Gutiérrez and María J. Ruedas Rama

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Granada (Spain), 2011.

III JORNADAS IBÉRICAS DE FOTOQUÍMICA

and

X CONGRESO DE FOTOQUÍMICA

Joint meeting of the specialized photochemistry groups of
the Spanish Royal Society of Chemistry (RSEQ) and the
Portuguese Society of Chemistry (SPQ)

Dear Colleagues and Friends,

Welcome to Granada for the **III Jornadas Ibéricas de Fotoquímica** (III-JIF). This conference is the tenth edition of a series of biennial meetings of the Spanish group of Photochemistry, **GRUFO**, of the **Real Sociedad Española de Química** (RSEQ), as well as the third edition of the joint meeting with the Portuguese Photochemistry subgroup of the **Sociedade Portuguesa de Química** (SPQ). Held for the first time here in Granada twenty years ago, in 1991, with the **I Reunión del Grupo de Fotoquímica**, this conference series has become one of the major photochemistry and photophysics forums of the Spanish and Portuguese scientific community.

The **III-JIF** will address all the modern aspects of photochemistry and photophysics, such as photochemical processes in biology; imaging; constrained systems; stereochemistry; singlet oxygen; chemical kinetics; coherent control; photocatalysis; energy transfer; photovoltaic; interstellar and atmospheric materials; laser development; modern spectroscopic methods; luminescent nanoparticles, etc. It has ensured the participation of scientist from highly qualified European groups in those fields, so the meeting will provide numerous possibilities for stimulating discussion and communications. We hope the scientific activities are very fruitful, and the conference works like a starting point for further collaborations between our groups.

Several cultural and social activities are also planned for the entertainment of the conference participants. You are invited to join the welcome reception at the terrace of the **ABBA Hotel**; the guided night visit to the **Alhambra**, the enchanting world-heritage palace; the typical lunch and trip to the south side of **Sierra Nevada**, the **Alpujarras**, and the banquet dinner at one of the most emblematic restaurants with breathtaking views of the **Alhambra**.

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I would like to point out the invaluable help from the members of the **Scientific Advisory Committee** for their support in putting together the exciting scientific sessions; the members of the **International Organizing Committee** for their assistance in publicizing the meeting and ensuring its success; and of course, the members of the **Local Organizing Committee** without whom the conference would not have been at all possible.

I wish also like to thank the **Institutions and companies** for their financial support. Please, visit the stands of the different companies at the poster exhibition area to get information on state-of-the-art instrumentation and technical advances. Finally, I am thanking **Viajes el Corte Inglés** and **UGR administration staffs** for the wonderful job they did.

So, please enjoy the conference!

Jose M^a Alvarez-Pez
Chairperson of the III Jornadas Ibéricas de Fotoquímica
Granada, July 21st, 2011.

III JORNADAS IBÉRICAS DE FOTOQUÍMICA

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GENERAL INFORMATION

Conference venue

The **III Jornadas Ibéricas de Fotoquímica** will take place at the **Faculty of Pharmacy**, at the **Cartuja Campus**, one of the University places in Granada. The **Faculty of Pharmacy** will kindly provide the use of the magnificent **Aula Magna** and the rest of its facilities. The **Aula Magna** is a comfortable venue with the latest audiovisual technology.

The Cartuja Campus is at walking distance from the hotels suggested by the organization (15-20 min walking). However, public transportation can be used:

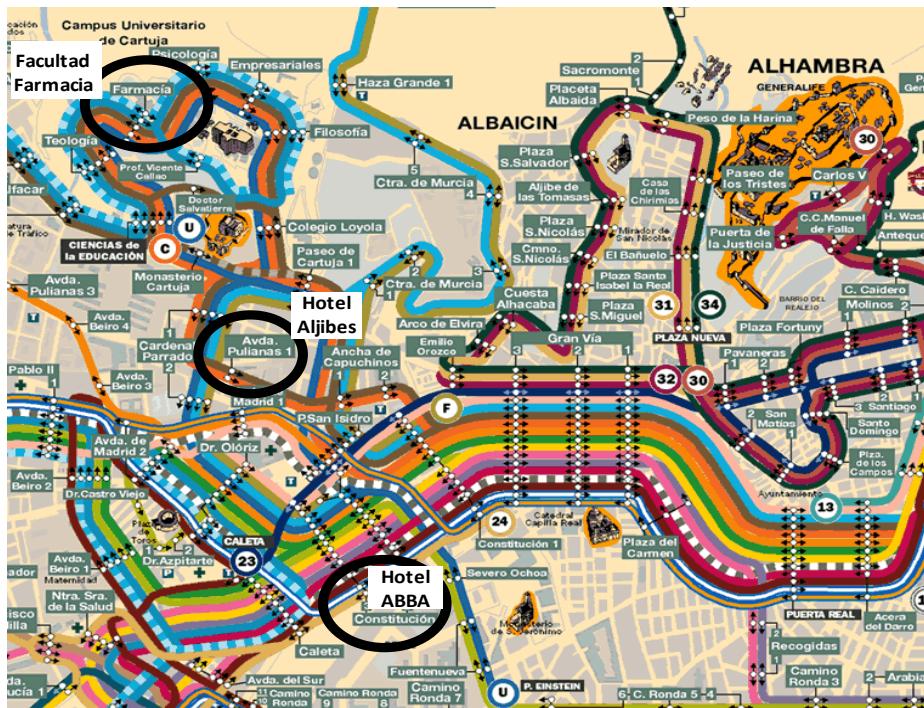
Bus: City buses number 8, 20, C, or U can be taken from different places around the city. Several stops are around the hotels.

Taxi: Several taxi stops are around the hotels (Avda. Constitución, Plaza de San Isidro, etc). For more information visit <http://www.granadadirect.com/transporte/taxis-granada>. Some taxi telephone numbers are provided:

Radio Taxi Granada: +34 958 280 654

Radio Taxi Genil: +34 958 132 323

Taxi Granada: +34 637 513 026



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Parking

Although the Faculty of Pharmacy is unable to provide public parking to attendees, there are parking lots located in the immediate area.

Registration

Participants can do the registration and pick up the materials and documentation on Monday 5th from 8:00 to 9:00 am at the main entrance of the Faculty of Pharmacy. Tickets for the working lunches, social activities, and conference banquet will be provided within the documentation.

Poster sessions

The poster sessions will be held at the main corridor of the Faculty (second floor), traditionally known by the students as the **M-30** corridor.

All posters must be on view during the morning on Monday 5th until 16:00 pm on Wednesday 7th in the **Exhibition Poster Area**. The poster boards will be numbered as in the abstract book. Pushpins or double-sided tape will be provided by the organization.

The presenting authors should present their communications on Monday 5th and Wednesday 7th from 14:30 to 16:00 pm. Coffee will be served during the poster sessions.

Working lunches

The lunches of Monday 5th and Wednesday 7th will be held at the **Neomudejar Hall** at the **Colegio Máximo**, a historic building reminiscent of the Mudejar style. Currently, the **Colegio Máximo** is the Faculty of Communication and Documentation and is also located at the Cartuja Campus, nearby the Faculty of Pharmacy (see map).



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Internet Access

A **computer room** is located in the first floor near the main entrance of the Faculty. This room will be specifically booked for the conference participants. A second computer room is nearby the Exhibition Poster Area, in the second floor. Attendees can access their email accounts for free on one of the available computers.

Wireless Internet Access

Attendees with their own laptops can access this service for free. There are several choices for wireless connection:

- **EDUROAM network:** Those participants from Institutions associated to the **EDUROAM network**, whose laptop computers are already configured for this connection, can connect indistinctly to the Wi-Fi networks **eduroam** or **cviugr-v2**.
- **Public Wi-Fi network:** In order to connect select the **cviugr** network. When browsing the internet you will be required to input the following login details:

User name: **grufo@invitados.ugr.es**

Password (note that the password is case sensitive): **Foto+Ugr2011**

Transportation to Granada airport

Bus: Airport bus service is available from different places around the city. The company is Autocares Jose Gonzalez, and the ticket fare is 3 €.

Bus stops (Granada → Airport): Exhibition and Conference Center – Puerta Real – Granada Cathedral – Gran Vía – Triunfo – Caleta – Bus Station – Airport.

Taxi: The Granada taxis also offer the Airport services. See above for the telephone numbers.

For more information about transportation to the airport visit
<http://www.granadadirect.com/transporte/aeropuerto-granada>.

Transportation to the social activities:

The transportation to the Alhambra, the Alpujarra and the banquet dinner is arranged by the organization.

Buses to **the conference banquet on Monday 5th** and the **Alhambra visit on Tuesday 6th** will pick up the attendees from the ABBA Hotel. Attendees staying at different hotels should allow some time to reach the pick up point.

Buses to the trip to the Alpujarras will depart from the Faculty of Pharmacy, just at the end of the scientific session. Please, reach the pick up point as soon as possible to avoid delays in the trip.

Hotel telephone numbers

ABBA Hotel: +34 958 807 807

Puerta de los Aljibes Hotel: +34 958 163 000

Aben-Humeya Hotel: +34 958 295 061

PRESENTATION

	Monday 5th	Tuesday 6th	Wednesday 7th	
8:00-9:00	REGISTRATION			
8:45-9:00	OPENING CEREMONY			
9:00-10:00	PL-1 Klenerman	9:00-10:00	PL-2 Kirsch-De Mesmaeker	9:00-9:35
10:00-10:35	INV-1 García-Moreno	10:00-10:35	INV-3 Prieto	9:35-10:10
10:35-11:00			COFFEE BREAK	10:10-10:30
11:00-11:20	OR-1 Baleizão	11:00-11:35	INV-4 Boens	11:00-11:20
11:20-11:40	OR-2 Pocoví-Martínez		OR-13 Descalzo	11:20-11:40
11:40-12:00	OR-3 Faria	11:35-11:55	OR-14 Ruedas-Rama	11:40-12:00
12:00-12:20	OR-4 Pérez-Lustres	11:55-12:15	OR-15 Aguilera-Sigalat	12:00-12:20
12:20-12:40	OR-5 Encinas	12:15-12:35		12:20-12:40
12:40-13:00	OR-6 Cerdán			12:40-13:00
13:00-14:30	LUNCH			13:00-14:30
14:30-16:00	POSTER SESSION			14:30-16:00
16:00-16:35	INV-2 Pérez-Inestrosa			16:00-16:35
16:35-16:55	OR-7 Durán-Sampedro			16:35-17:10
16:55-17:15	OR-8 Collado			
17:15-17:35	OR-9 Dí Nunzio			17:10-17:30
17:35-17:55	OR-10 López-Gejo			17:30-17:50
17:55-18:15	OR-11 Saini			17:50-18:10
		TRIP TO THE ALPUJARRAS		
21:00	CONFERENCE BANQUET AT 'LA CHUMBERA'	21:00	NIGHT VISIT TO THE ALHAMBRA	
			GRUFO BOARD MEETING	

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III JORNADAS IBÉRICAS DE FOTOQUÍMICA – CONFERENCE PROGRAM

MONDAY 5TH

8:00 – 9:00 **Conference Registration**

8:45 – 9:00 Opening ceremony

SESSION 1. Chairman: Angel Orte (U. Granada)

9:00 – 10:00 Plenary Talk: **David Kleinerman** (U. Cambridge, U.K.). *New biological insights from single molecule studies.*

10:00 – 10:35 Memorial Talk for Dr. Roberto Sastre: **Inmaculada García-Moreno** (C.S.I.C., Spain). *Roberto Sastre: Creativity in photopolymers.*

10:35 – 11:00 COFFEE BREAK

SESSION 2. Chairwoman: Inmaculada García-Moreno (C.S.I.C.)

11:00 – 11:20 OR-1: Carlos Baleizão (IST, UTL, Portugal). *The Brightest Fullerene: A New Isotope Effect in Molecular Fluorescence and Phosphorescence.*

11:20 – 11:40 OR-2: Salvador Pocoví Martínez (U. Valencia, Spain). *Controlled UV-C Light-Induced Fusion of Thiol-Passivated Gold Nanoparticles.*

11:40 – 12:00 OR-3: Joaquim L. Faria (U. Porto, Portugal). *When carbon meets light: enhancing photocatalytic activity of TiO₂ by introducing carbon nanotubes.*

12:00 – 12:20 OR-4: J. Luis Pérez-Lustres (U. Santiago de Compostela, Spain). *Photoisomerisation around a fulvene double bond. Coherent population transfer to the electronic ground state?*

12:20 – 12:40 OR-5: Susana Encinas (U.P.V., Spain). *Sunscreens as feasible oxygen acceptors in the photo-deoxygenation of heterocyclic N-oxides.*

12:40 – 13:00 OR-6: Luis Cerdán (C.S.I.C., Spain). *Studies on stimulated emission in dye-doped polymer thin films.*

13:00 – 14:30 LUNCH AT THE NEOMUDÉJAR HALL (COLEGIO MÁXIMO)

14:30 – 16:00 POSTER SESSION

PRESENTATION

SESSION 3. Chairman: Pedro Campos (U. La Rioja)

16:00 – 16:35 Memorial Talk for Prof. Rafael Suau: **Ezequiel Pérez-Inestrosa** (U. Málaga, Spain). *Photochemical Electron Transfer: from synthetic uses to applications under molecular Boolean logic.*

16:35 – 16:55 OR-7: Gonzalo Durán Sampedro (U.C.M., Spain). *Fluorescence and Laser Performance of Fluorinated BODIPY Dyes.*

16:55 – 17:15 OR-8: Daniel Collado (U. Malaga, Spain). *Photophysical processes in bicomophoric Naphthalimide-BODIPY systems.*

17:15 – 17:35 OR-9: Maria Rosaria di Nunzio (U. Castilla-La Mancha). *Energy transfer from caged Topotecan (a potent anti-cancer drug) to a Rhodamine-cyclodextrin nanocarrier.*

17:35 – 17:55 OR-10: Juan López-Gejo (U.C.M., Spain). *Luminescent polymer nanofibers with high oxygen permeability for photochemical chemical sensing.*

17:55 – 18:15 OR-11: Vipin K. Saini (IST, UTL, Portugal). *Polyelectrolyte-assisted functionalization of carbon nanotubes with ordered assemblies of a water soluble porphyrin.*

21:00 CONFERENCE BANQUET AT ‘LA CHUMBERA’

TUESDAY 6TH

SESSION 4. Chairman: Guillermo Orellana (U. Complutense Madrid)

9:00 – 10:00 Plenary Talk: **Andrée Kirsch-De Mesmaeker** (U. L. Brussels, Belgium). *Mechanisms and applications of photobridging of biomolecules by Ru(II) complexes.*

10:00 – 10:35 Invited Talk: **Manuel Prieto** (U. T. Lisboa, Portugal). *Advanced FRET methodologies in membrane biophysics.*

10:35 – 11:00 COFFEE BREAK

SESSION 5. Chairman: Joaquim L. Faria (U. Porto)

11:00 – 11:35 Invited Talk: **Noël Boens** (K.U. Leuven, Belgium). *BODIPY.*

11:35 – 11:55 OR-13: Ana Belén Descalzo (U.C.M., Spain). *Luminescent Silica Nanoparticles Engineered for Enrofloxacin Sensing based on FRET.*

11:55 – 12:15 OR-14: María J. Ruedas-Rama (U. Granada, Spain). *Quantum Dot as photoluminescence lifetime-based nanosensors.*

12:15 – 12:35 OR-15: Jordi Aguilera-Sigalat (U. Valencia, Spain). *Methodology to obtain highly fluorescent organic- and water-soluble CdSe/ZnS core-shell quantum dots capped with thiols.*

III JORNADAS IBÉRICAS DE FOTOQUÍMICA

12:35 EXCURSION TRIP TO THE ‘ALPUJARRAS’. LUNCH AT PAMPANEIRA.

21:00 NIGHT VISIT TO THE ALHAMBRA

WEDNESDAY 7TH

SESSION 6. Chairwoman: Flor Rodríguez-Prieto (U. Santiago de Compostela)

9:00 – 9:35 Invited Talk: **Sérgio J. Seixas de Melo** (U. Coimbra, Portugal). *Photophysics and Excited State Behavior of Organic Molecules Involving Two and Three Interconverting Excited Species.*

9:35 – 10:10 Invited Talk: **Cristina Flors** (U. Edinburgh, U.K.). *Fluorescence photoswitching in DNA: applications in advanced fluorescence microscopy.*

10:10 – 10:30 OR-16: Mercedes Novo (U. Santiago de Compostela, Spain). *Association Dynamics of DNA Minor Groove Binders.*

10:30 – 11:00 COFFEE BREAK

SESSION 7. Chairman: António L. Maçanita (IST, U. T. Lisboa)

11:00 – 11:20 OR-17: María J. Marin Altaba (U. East Anglia, U.K.). *Gold nanoparticles functionalised with PET-based fluorescent probes for intracellular measurements of pH.*

11:20 – 11:40 OR-18: Cristina Martín (U. Castilla-La Mancha, Spain). *Study of the fluorescence enhancement of stable core-shell silica nanoparticles using single molecule emission spectroscopy.*

11:40 – 12:00 OR-19: Ruperto Bermejo (U. Jaen, Spain). *New magnetic-luminescent nanoparticles composed by ferritin with linked phycocyanins and phycoerythrins.*

12:00 – 12:20 OR-20: Marina Blanco-Lomas (U. La Rioja, Spain). *Light-activated biomimetic molecular switches.*

12:20 – 12:40 OR-21: Patricia Remón (U. Huelva, Spain). *Molecular logic switching with spiropyran-fluorophore dyads.*

12:40 – 13:00 OR-22: Jorge Bañuelos Prieto (E.H.U., Spain). *Halogenated BODIPY as generators of singlet oxygen.*

13:00 – 14:30 LUNCH AT THE NEOMUDÉJAR HALL (COLEGIO MÁXIMO)

14:30 – 16:00 POSTER SESSION

PRESENTATION

SESSION 8. Chairman: Ulises Acuña (C.S.I.C.)

16:00 – 16:35 Invited Talk: **Asier Longarte** (E.H.U., Spain). *Photostability of aromatic chromophores: ultrafast dynamics involving $\pi\sigma^*$ electronic states.*

16:35 – 17:10 Invited Talk: **Gustavo de Miguel** (U. Castilla-La Mancha, Spain). *Femtosecond dynamics of squaraine molecules with potential application as sensitizers in DSSCs.*

17:10 – 17:30 OR-23: Virginia Martín (C.S.I.C., Spain). *New 8-amino-BODIPY derivatives: surpassing laser dyes at blue-edge wavelengths.*

17:30 – 17:50 OR-24: César A. T. Laia (REQUIMTE, Portugal). *Photophysics of Ionic Liquids.*

17:50 – 18:10 OR-25: Obis D. Castaño (U. Alcalá, Spain). *Non-vertical Triplet-Triplet Energy Transfer in condensed phase: definition and quantification of the reaction coordinate.*

18:10 – 18:15 CONCLUDING REMARKS

18:15 – 18:30 GRUFO BOARD MEETING

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III JORNADAS IBÉRICAS DE FOTOQUÍMICA –
ABSTRACTS

PLENARY TALKS

PLENARY TALKS

PL-1 – New biological insights from single molecule studies

David Kleinerman

Department of Chemistry, Cambridge University, CB2 1EW, Cambridge (United Kingdom)

e-mail: dk10012@cam.ac.uk

Single molecule fluorescence studies have now reached a stage where they can provide new insights into important biological problems. After presenting the principles of these methods, I will give three examples from our research. Firstly we have used single molecule fluorescence to detect and analyse the low concentrations of soluble oligomers present during the aggregation reaction of amyloid beta and alpha synuclein, proteins responsible for Alzheimer's and Parkinson's disease respectively. This has enabled us to gain new insights into the molecular mechanism of aggregation. Secondly we have imaged individual proteins on the surface of a live T cell to elucidate the initial molecular events that lead to T-cell triggering, which underpins the adaptive immune response. Finally, I will describe how fundamental science aimed at watching single molecules incorporating nucleotides into DNA gave rise to a new rapid method to sequence DNA that is now widely used.

PL-2 – Mechanisms and Applications of Photobridgings of Biomolecules by Ru(II) complexes.

Andrée Kirsch - De Mesmaeker

Department of Chemistry, Faculty of Sciences, 50 av. F.D. Roosevelt, CP 160/08, Université libre de Bruxelles, 1050 Brussels, Belgium

e-mail: akirsch@ulb.ac.be

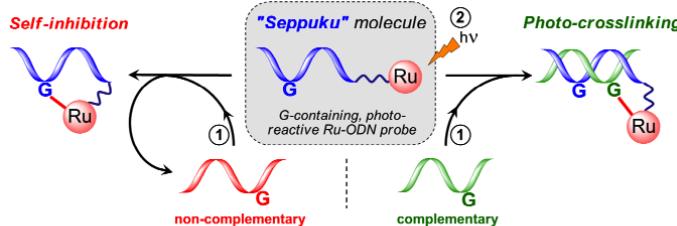
In the first part of the lecture, we will examine the main photochemical characteristics of the Ru(II) complexes that contain at least two tetraazaphenanthrene ligands (TAP). In the second part we will develop some interesting applications of these complexes based on these special properties.

The excited $^3\text{MLCT}$ states of the Ru-TAP complexes are able to extract an electron from guanine (G) bases of DNA and from tryptophan residues of polypeptides. The dynamics of these photo-induced electron transfers (PET) will be briefly discussed under pulsed illumination, in the nano- and pico-second time domains.

It was shown that these PET processes lead after several reaction steps, to formation of an adduct of the metallic compound on the G bases or on the Trp residues. Moreover, very interestingly, it was also observed that bi-adducts, i.e. the addition of two G or two Trp units on the same Ru(II) complex can also be produced.

The possible mechanisms of formation of these bi-adducts will be discussed thanks to laser-induced transient absorption experiments carried out from the pico- to the milli-second time domain.

Finally we will discuss different applications of the photo-induced productions of the above-mentioned mono- and bi-adducts in order to photo-crosslink oligonucleotides and oligopeptides. Thus we will describe the possible use of these complexes as molecular tools in biochemistry or biology and as photodrugs, efficient in gene silencing. In this case, the use of "Seppuku" Ru-oligonucleotides will be illustrated [1].



Application in gene silencing

[1] S. Le Gac, S. Rickling, P. Gerbaux, C. Moucheron, and A. Kirsch - De Mesmaeker, *Angewandte Chem.*, **48**, 1122-1125 (2009).

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ABSTRACTS

INVITED TALKS

INVITED TALKS

INV-1 – Roberto Sastre: Creativity in Photopolymers

I. García-Moreno

Instituto de Química Física “Rocasolano”, CSIC, Serrano 119, 28006, Madrid, Spain

e-mail: i.garcia-moreno@iqfr.csic.es

Roberto Sastre (1944-2010) received his Ph.D. in Chemistry from the Universidad Complutense de Madrid, Spain. He was Professor of Research at Consejo Superior de Investigaciones Científicas (CSIC), in the Instituto de Ciencia y Tecnología de Polímeros, Madrid. He was also a visiting scientist at Catholic University of Lovaina, Belgium; Institute of Macromolecular Chemistry, Prague, Czechoslovakia; Ecole National Supérieur d'Arts et Matiers, Paris, France, and Universidad Católica de Chile, Santiago de Chile. Roberto Sastre authored more than 200 papers in refereed journals and over 20 patents. His research focused on: photophysics and photochemistry of polymers and photoinitiators of polymerization, biomaterials, organic chemistry, synthesis and characterization of optical materials, holographic recording in photopolymers, laser ablation of materials, and solid-state dye lasers.

Although debilitated in his last year by his battle against lung cancer, Prof. Sastre remained active until near the end. Towards the end of his career his work was more focused on technological applications, and made significant contributions to the development of organic-inorganic hybrid materials for optoelectronic (bulk solid-state and waveguide lasers based on dyes incorporated into nonnanostructured media) and biophotonic (dental bone cements) applications.

Selected Publications:

- [1] J. Catalán, F. Fabero, R. Claramunt, M.D. Santa-María, M. Forces, M. Martínez-Ripoll, J. Elguero, R. Sastre, New ultraviolet stabilizers: 3 and 5 (2'hydroxyphenyl) pyrazoles, *J. Am. Chem. Soc.*, **114**, 5039-5048 (1992).
- [2] R. Mallavia, F. Amat, R. Sastre, Synthesis and evaluation as visible light polymerization photoinitiator of a new Eosin ester with a O-benzoyloxime group, *Macromolecules*, **27**, 2643-2646 (1994).
- [3] R.M. Trigo, M.D. Blanco, J.M. Teijón, R. Sastre, Anticancer drug, Ara-C, release from PHEMA hydrogels, *Biomaterials*, **15**, 1181-1186 (1994).
- [4] R. Sastre and A. Costela, Polymeric solid-state dye lasers, *Adv. Mater.*, **7**, 198-204 (1995).
- [5] C. Peniche, W. Argüelles, N. Davidenko, R. Sastre, A. Gallardo, J. San Román, Self-curing membranes of chitosan/PAA IPNs obtained by radical polymerization: preparation, characterization and interpolymer complexation, *Biomaterials*, **20**, 1869-1878 (1999).
- [6] A. Aspée, O. García, L. Maretti, R. Sastre, J. C. Scaiano, Free radical reactions in PMMA films monitored using a pre-fluorescent Quinoline-Tempo sensor, *Macromolecules*, **36**, 3550-3556 (2003).
- [7] O. García, R. Sastre, D. del Agua, A. Costela, I. García-Moreno, New Fluorinated Polymers doped with BODIPY chromophore as highly efficient and photostable optical materials, *Chem. Mat.*, **18**, 601-602 (2006).
- [8] I. García-Moreno, F. Amat, M. Liras, A. Costela, L. Infantes, R. Sastre, F. López-Arbeloa, J. Bañuelos-Prieto, I. López-Arbeloa, Structural Changes in the BODIPY Dye PM 567 Enhancing their Laser Action in Liquid and Solid Media, *Adv. Func. Mater.*, **17**, 3088-3098 (2007).

INVITED TALKS

- [9] M. Liras, J. Bañuelos, M. Pintado, F. López-Arbeloa, I. García-Moreno, A. Costela, L. Infantes, R. Sastre, F. Amat, Synthesis, Photophysical Properties and Laser Behavior of 3-amino and 3-Acetamido BODIPY Dyes, *Org. Lett.*, **9**, 4183-4186 (2007).
- [10] L. Martín, O. Osso, S. Ricart, A. Roig, O. García, R. Sastre, Organo-modified silica aerogels and its implications on the material hydrophobicity and mechanical properties, *J. Mater. Sci.*, **18**, 207-213 (2008).
- [11] O. García, L. Garrido, R. Sastre, A. Costela, I. García-Moreno, Synthesis strategies on hybrid materials improving properties for optoelectronic applications, *Adv. Func. Mater.*, **18**, 2017-2025 (2008).
- [12] A. Costela, O. García, L. Cerdán, I. García-Moreno, R. Sastre, Amplified spontaneous emission and optical gain measurements from pyrromethene 567- doped polymer waveguides and quasi-waveguides, *Opt. Express*, **16**, 7023-7036 (2008).
- [13] A. Costela, I. García-Moreno, L. Cerdan, V. Martín, O. García, R. Sastre, Dye-doped POSS solutions: random nanomaterials for laser emission, *Adv. Mat.*, **21**, 1-4 (2009).
- [14] R. Sastre *et al.*, Dye-doped polyhedral oligomeric silsesquioxane (POSS)-modified polymeric matrices for highly-efficient and photostable solid-state dye lasers, *Adv. Funct. Mater.*, **19**, 3307-3319 (2009).

INV-2 – Photochemical Electron Transfer: from synthetic uses to applications under molecular Boolean logic

Ezequiel Perez-Inestrosa

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In this session, the Scientific, University and Photochemical communities pay homage to the memory of Professor Dr Rafael SUAU, who died on November 11th, 2010. For all those who knew him he will be remembered as a teacher and an exceptional scientist who took Spanish organic photochemistry to the highest levels of international renown.

Through the importance of his scientific legacy and his long-term vision, Rafael Suau was a remarkable scientist. Most of his contributions are in the area of synthetic organic photochemistry, but travels toward the information processing. He made emerge Phthalimides as showing a considerable variety of photochemical behaviour, and many of the reactions were put to good use in the synthesis of heterocyclic compounds applied to natural products chemistry. By the development of photochemical aromatic hydroxylation process he demonstrates also the value of the photochemical reactivity of heterocyclic *N*-oxides.

The example of his life suggests that science is not just a job, a profession, let alone a sheer title, but more than anything a kind of life attitude. Being a man of deep erudition, he exerted his influence not just by the power of words but also through his vital example, a way of living and relentless sense of duty, as well.

In addition to his professional career as a leading specialist, Rafael Suau will be missed by all those who had the good fortune to know and appreciate his abilities, his honesty and his scientific rigour, his simplicity, his deep humanity and his indestructible friendship.

INVITED TALKS

INV-3 – Advanced FRET methodologies in membrane biophysics

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Förster resonance energy transfer (FRET), in most applications used as a “spectroscopic ruler”, allows a direct determination of the donor-acceptor intermolecular distance. However, in membranes the situation becomes complex, since around each donor there is an ensemble of acceptors at non-correlated distances. State-of-the-art methodologies for this situation will be presented, that involve model derivation and fitting to time-resolved fluorescence data. This powerful approach can be used to study the occurrence of phase separation (“lipid rafts” and other type of membrane domains), allowing their detection as well as size characterization. Formalisms for studying lipid-protein and protein-protein interactions according to specific topologies will also be addressed. The advantages and added complexity of a specific type of FRET (energy homo-transfer or energy migration) will be described, as well as applications of FRET under the microscope, namely the study of lipid-protein amyloid like fibers.

Acknowledgement. This work was supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) projects references PTDC/QUI-BIQ/099947/2008, FCOMP-01-0124-FEDER-010787 (FCT PTDC/QUI-QUI/098198/2008) and PTDC/QUI-BIQ/112067/2009

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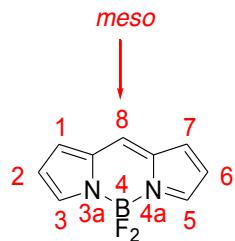
BODIPY

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This lecture covers the advances made using the 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) scaffold as fluorophore used in various fields of modern science and medicine. Nowadays BODIPY is a very popular fluorophore with many possible applications (dyes for biological labeling, for electroluminescent devices, as tunable laser dyes, as potential candidates for solid-state solar concentrators, as fluorescent switches, and fluorophores in sensors and labels). The robustness against light and chemicals, the relatively high molar absorption coefficients $\epsilon(\lambda)$ and fluorescence quantum yields Φ , negligible triplet-state formation, narrow emission bandwidths with high peak intensities, good solubility, resistance towards self-aggregation in solution, excitation/emission wavelengths in the visible spectral region (≥ 500 nm), and fluorescence lifetimes τ in the nanosecond range all contribute to the appeal of these interesting compounds. Moreover, their spectroscopic and photophysical properties can be fine-tuned by attachment of ancillary residues at the appropriate positions of the difluoroboron dipyrromethene core. In this lecture we will show the recent synthetic advances in postfunctionalization of the BODIPY core and the spectroscopic / photophysical properties of the dyes as a function of the substitution pattern. The wide versatility of synthetic pathways to the BODIPY class of fluorophores allows the creation of a perfect fit between the structure of the dye and its desired spectroscopic and photophysical characteristics. Application of BODIPY as fluorescent reporter unit in a pH sensor will be discussed.



the "BODIPY core" and

its IUPAC numbering system

Figure 1. Representation of the BODIPY framework with the numbering scheme shown. All the positions of the BODIPY core are possible sites for functionalization.

INVITED TALKS

INV-5 – Photophysics and Excited State Behavior of Organic Molecules Involving Two and Three Interconverting Excited Species

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In recent years we have been heavily engaged in the characterization of the excited states of organic molecules such as indigo, pyrene-labeled polymers and oligomers, conjugated organic polymers and oligomers and hydroxycoumarins [1-4]. The mechanisms involved in the deactivation of their excited species include, among others, proton transfer, energy transfer, excimer formation and conformational relaxation. These all have in common excited state kinetic schemes that can involve two or three coupled species (special cases where four excited species are involved are reduced to a three-state system plus an isolated species).

Examples of these systems, including the determination of all deactivation pathways (quantum yields and lifetimes), identification of the species involved, analysis of excited state kinetics, will be given together with the relevance of these mechanisms to the understanding of their photophysical properties. In particular these will include 1) indigo where the high value of its internal conversion yield, together with the (double exponential) nature of the fluorescence decays links its high stability with the excited state proton transfer between the N-H and C=O groups [2]; 2) pyrene-labeled polymers, in which the number of species (three to four) is dependent on the nature (and size) of the polymer chain and can be used to probe the dynamics of the systems [1,3] and 3) conjugated organic polymers and oligomers showing the competitive processes of energy migration and conformational relaxations [3,4].

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Acknowledgement. I am grateful to POCI (project PTDC/QUI-QUI/099388/2008), Fundação para a Ciência e a Tecnologia (FCT) and FEDER for further funding.

INV-6 – Fluorescence photoswitching in DNA: applications in advanced fluorescence microscopy

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Fluorescence photoswitching is at the core of newly developed fluorescence microscopy techniques. In particular, photoswitching is crucial for super-resolution fluorescence microscopy, which can provide images with an order of magnitude improvement in spatial resolution compared to conventional fluorescence microscopy. In super-resolution fluorescence microscopy, the ability to label the structures of interest with photoswitchable or photoactivatable fluorophores in high density is critical. While this is easily achievable for proteins, labelling DNA with a high density of photoswitchable fluorophores is still a challenge. Intercalating and minor-groove binding cyanine dyes in combination with special buffers that induce photoblinking have been used to image isolated and cell DNA using super-resolution microscopy [1]. This approach yields super-resolution images of unspecifically stained DNA with a spatial resolution below 40 nm. On the other hand, controllable fluorescence photoswitching in sequence-specific DNA fragments can be also achieved using a different strategy. Newly evolved DNA polymerases allow the efficient incorporation of fluorophores into fragments of up to 1 kb [2] and are a promising alternative to achieve controllable fluorescence photoswitching in DNA fragments. Moreover, reversible and reproducible photoswitching in DNA also enables other advanced microscopy modalities such as optical-lock in detection imaging, which enhances the contrast in fluorescence imaging [3]. The combination the above techniques have great potential to study the structure of chromosomes at the nanoscale.

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Acknowledgement: This work has been supported by The Royal Society.

INV-7 – Photostability of aromatic chromophores: ultrafast dynamics involving $\pi\sigma^*$ electronic states

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The photochemical and photophysical properties of natural chromophores containing heteroatoms (N, O), are highly influenced by the existence of $\pi\sigma^*$ type dark states in the vicinity of the strongly allowed $\pi\pi^*$ transitions that permit the electronic excitation of the molecule. These $\pi\sigma^*$ states are usually Rydberg character transitions involving the 3s orbital of the heteroatom that present dissociative character along the X-H (X: O, N) coordinate. The dynamics on the $\pi\sigma^*$ electronic surfaces have a great influence in very relevant photoinduced phenomena like photodissociation, charge transfer reactions, or even internal conversion in biomolecules as DNA bases or amino acids [1]. This dynamics, which presents a very complicated nature, results of the non-adiabatic coupling (interaction between the electronic and vibrational coordinates) of the $\pi\sigma^*$ state with the nearby $\pi\pi^*$ transitions and the ground state of the molecule. Our group is interested in understanding the ultrafast relaxation mechanisms involving $\pi\sigma^*$ surfaces in a set of isolated aromatic chromophores including: aniline, indole, phenol or pyrrole. In addition we also aim to unravel the role of the solvent degrees of freedom on the dynamical processes originated on the $\pi\sigma^*$ states by conducting experiments on the nano-solvation environment of molecular clusters.

The dynamical signature of the $\pi\sigma^*$ state has been tracked directly on the parent molecule photoexcited in the 300-235 nm range, by multiphoton delayed ionization at several wavelengths. The experiments carried out have allowed us to follow the relaxation of the system up to nanoseconds delays with femtosecond resolution. The study provides a clear view of the importance of $\pi\sigma^*$ states in the photochemistry of aromatic chromophores in the range of the studied excitation wavelengths.

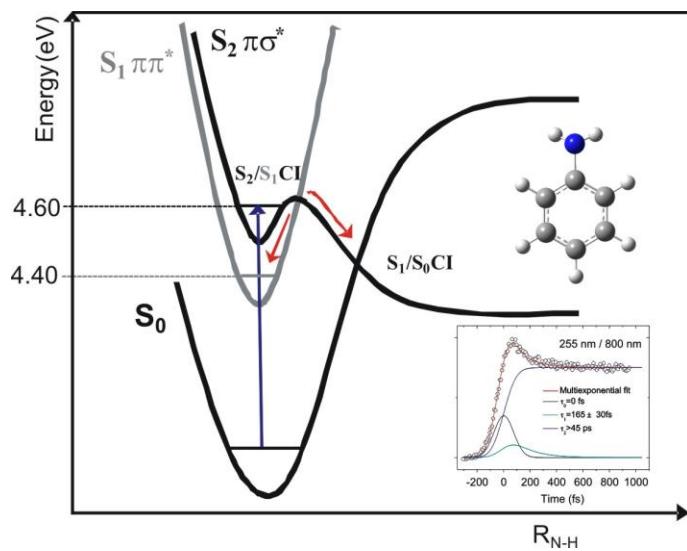


Figure 1. Scheme and time dependent signal corresponding to the relaxation corresponding to the relaxation of aniline after excitation at 255 nm

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INV-8 – Femtosecond dynamics of squaraine molecules with potential application as sensitizers in DSSCs

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The photodynamics of three types of squaraines (SQs) [1] molecules in solution, deposited onto quartz substrates and embedded in a TiO₂ nanoparticle thin film [2] have been studied by means of steady-state and time-resolved absorption techniques with the aim of a better understanding of their excited state properties. In pure SQs thin films, the formation of two species at the excited state, monomer and H- or J-aggregates was proved. Non-exponential fit of the experimental time profiles together with the power-dependence of the transient absorption signal makes us to propose a singlet-singlet annihilation process to account for the rapid deactivation of the aggregate excited state. In SQs embedded in TiO₂ nanoparticles thin films, we only detected the formation of H-aggregates and monomer species. Femtosecond transient absorption measurements revealed a charge injection rate constant quite similar for the three SQs molecules. However, rate constant for charge recombination turned out to be one order of magnitude higher for the unsymmetrical SQ with only one carboxylic group, $k_{cr} = 1.5 \times 10^6 \text{ s}^{-1}$ respect to the symmetrical SQs with two carboxylic groups

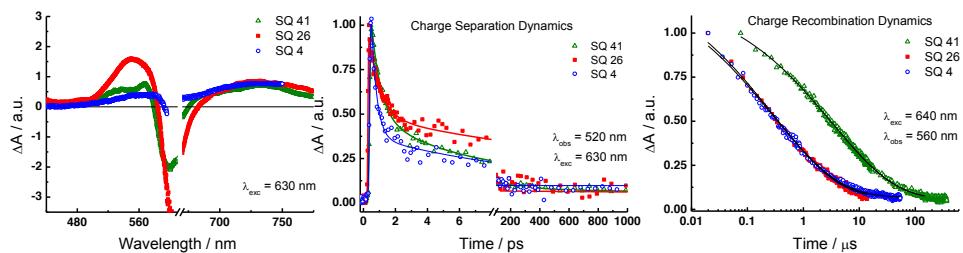


Figure 1. Transient absorption spectra at 1 ns (left), time profiles at 520 nm, (middle) and charge recombination dynamics (right), upon excitation at 640 nm of SQ 4 (blue line), SQ 26 (red line) and SQ 41 (green line) embedded in TiO₂ nanoparticle thin films.

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III JORNADAS IBÉRICAS DE FOTOQUÍMICA –
ABSTRACTS

ORAL COMMUNICATIONS

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OR-1 – The Brightest Fullerene: A New Isotope Effect in Molecular Fluorescence and Phosphorescence

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The isotopic composition of a fluorophore may have an effect on those photophysical properties that depend on the rate of radiationless transitions. The effect is well-documented for some aromatic molecules [1], which upon deuteration show a significant decrease in the internal conversion (IC) rate constant and an important increase in the triplet lifetime. This results from the lower frequency of the C–D normal modes as compared to the C–H ones, and is thus a nuclear mass effect. No photophysical studies exist on the effect of replacement of ^{12}C (natural abundance 99%) by ^{13}C (natural abundance 1%) in luminescent molecules. Compared to the change in effective reduced mass that occurs upon deuteration, the effect should be minor to negligible. Furthermore, it is the carbon–hydrogen normal modes that are usually dominant in nonradiative processes.

A second type of isotopic effect is known: the magnetic isotope effect [2]. It occurs by means of electron–nuclear hyperfine coupling, and under favourable conditions it may influence slow intersystem crossing (ISC) rates. In radical recombination reactions, the effect has been shown to occur with ^{13}C , an isotope with nuclear spin 1/2 (in contrast, ^{12}C has zero nuclear spin) [2]. This effect is however unknown for excited states.

Fullerenes C_{60} , C_{70} , and some of their derivatives exhibit an important thermally activated delayed fluorescence (TADF) [3]. In the TADF mechanism, intersystem crossing (ISC) from S_1 to the triplet manifold (T_1 or a higher triplet) is followed by a second ISC from T_1 back to S_1 , and then by fluorescence emission. The cycle $\text{S}_1 \rightarrow \text{T}_1 \rightarrow \text{S}_1$ may repeat itself a number of times (up to nearly 170 for the molecule reported herein) before fluorescence finally takes place [4]. TADF is only significant when oxygen is absent or present in very low concentrations, otherwise the triplet state is quenched. Temperature is also an important parameter, because the number of $\text{S}_1 \rightarrow \text{T}_1 \rightarrow \text{S}_1$ cycles increases with the increase of temperature [4]. Recently, outstanding temperature [5–6] and oxygen [7–8] fluorescence sensors based on the TADF of C_{70} were reported.

Herein, we describe the very significant effect of ^{13}C enrichment on the delayed fluorescence of fullerenes C_{60} and C_{70} [9]. Substitution of ^{12}C by ^{13}C in C_{70} leads to major changes in its delayed fluorescence and phosphorescence properties. Delayed fluorescence lifetime (τ_{DF}) as a function of delayed fluorescence intensity ($I_{\text{DF}}/I_{\text{PF}}$) is shown in Figure 1 for $^{12}\text{C}_{70}$ and $^{13}\text{C}_{70}$ in polystyrene, and from the linear fit to the experimental points it is possible to obtain the quantum yield of triplet formation: 0.994 for $^{13}\text{C}_{70}$ and 0.990 for $^{12}\text{C}_{70}$. The hitherto unknown effect of ^{13}C on molecular luminescence, also observed for C_{60} , decreases the internal conversion and $\text{T}_1 \rightarrow \text{S}_0$ intersystem crossing rates by a mass effect, and increases

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the $S_1 \leftarrow T_1$ back intersystem crossing rate by a nuclear magnetic effect. A small increase (0.4%) in the quantum yield of triplet formation leads to the doubling of the high-temperature fluorescence quantum yield. As a consequence, $^{13}\text{C}_{70}$ is by far the brightest fullerene known, attaining a maximum fluorescence quantum yield of 9%. This upper value results from a large number of excited-state cycles of the type $S_1 \rightarrow T_1 \rightarrow S_1$ (as many as 170, on average) that increase the probability of decay through fluorescence. The strong delayed fluorescence intensities and long delayed fluorescence lifetimes of $^{13}\text{C}_{70}$ render this isotopologue a serious candidate for optical oxygen sensors with unprecedented detection limits at the ppbv level.

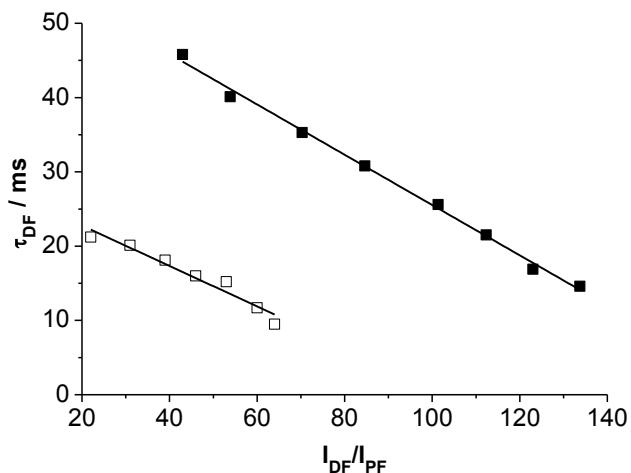


Figure 1. Delayed fluorescence lifetime (τ_{DF}) as a function of delayed fluorescence intensity ($I_{\text{DF}}/I_{\text{PF}}$) for $^{12}\text{C}_{70}$ (empty) and $^{13}\text{C}_{70}$ (filled) in polystyrene. The solid lines correspond to the linear fit to the data.

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OR-2 – Controlled UV-C Light-Induced Fusion of Thiol-Passivated Gold Nanoparticles

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Metal nanoparticles (MNPs) have unique optical and electronic properties that are not available in either molecules or bulk solids [1,2].

Thiol-passivated gold nanoparticles (AuNPs) of a relatively small size, either decorated with chromophoric groups, such as a phthalimide (Au@PH) and benzophenone (Au@BP), or capped with octadecanethiol (Au@ODCN) have been synthesized and characterized by NMR and UV-vis spectroscopy as well as transmission electron microscopy (TEM).

These NPs were irradiated in chloroform at different UV-wavelengths using either a nanosecond laser (266 and 355 nm, ca. 12 mJ/pulse, 10 ns pulse) or conventional lamps (300 nm < λ < 400 nm and ca. 240 nm < λ < 280 nm) and the new AuNPs were characterized by X-ray and UV-vis spectroscopy, as well as by TEM.

Laser irradiation at 355 nm led to NP aggregation and precipitation, while the NPs were photostable under UV-A lamp illumination. Remarkably, laser excitation at 266 nm induced a fast (minutes time-scale) increase in the size of the NPs, producing huge spherical nanocrystals, while lamp-irradiation at UV-C wavelengths brought about nanonetworks of partially fused NPs with a larger diameter than the native NPs.

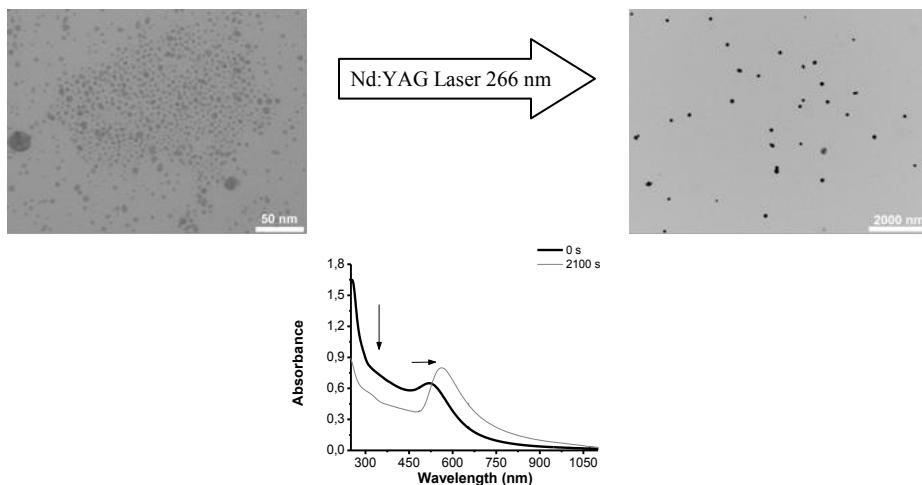


Figure 1. Irradiation of Au@BP with a ND:YAG laser at 266 nm.

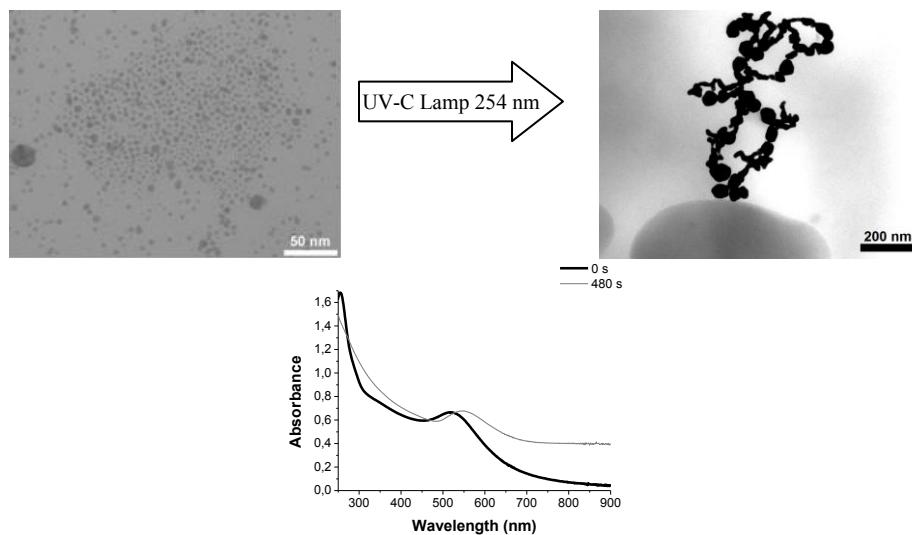


Figure 2. Irradiation of Au@BP with a UV-C lamp at 254 nm.

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Acknowledgement. We thank MEC (Project CTQ2008-06777-CO2-01, contract granted to S. P-M), GVA (Project ACOMP/2011/269).

OR-3 – When carbon meets light: enhancing photocatalytic activity of TiO₂ by introducing carbon nanotubes

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Carbon materials have been widely used in heterogeneous catalysis due to their extraordinary mechanical and electronic properties. In most applications carbon materials, and most particularly activated carbons, have been used as supports for active catalytic phases mostly because their resistance to acid/basic media, possibility to control, up to certain limits, the porosity and surface chemistry and easy recovery of precious metals by support burning resulting in a low environmental impact. With the arising of the era of nanoscience and nanotechnology, carbon nanostructures like nanofibers and nanotubes have gained an increased interest by the scientific community. Since they were discovered by Iijima [1] carbon nanotubes (CNT) have been extensively employed in a wide range of applications from energy storage to electronics and catalysis. Particularly in the field of photocatalysis, CNT have been used in the preparation of hybrid materials, based on its combination with metal oxides, possessing not only the properties of each component but also aiming at the creation of a synergistic effect between both phases.

TiO₂ has always been one of the best candidate materials for photocatalytic applications due to its photophysical and photochemical properties, its relative nontoxicity, and long-term thermodynamic stability. A great effort has been put to enhance the photocatalytic properties of TiO₂, mostly in what concerns to its use under visible light conditions and ultimately under solar irradiation. The mixture of TiO₂ with other types of semiconductors, TiO₂ doping with metals and non-metals, and recently the synthesis of hybrid materials constituted by TiO₂ and carbon nanostructures, have showed to produce an enhancement on the performance of the semiconductor when irradiated in the visible spectral range.

Here we present a review of the work that is being performed in our research group on the preparation, characterization and testing of TiO₂-CNT composite materials for photocatalytic applications. Photocatalytic properties of TiO₂-CNT materials may be tailored towards a specific application by varying several critical aspects such as preparation procedure, type of TiO₂, TiO₂ to CNT mass ratio, and CNT functionalization. Although the most usual method for TiO₂-CNT composites production is the sol-gel route, hydrothermal procedure can also been successfully used [2]. The obtained materials are generally constituted by TiO₂ nanoparticles bounded to the surface of the CNT or by CNT embedded in a TiO₂ matrix (Fig. 1). The morphology of TiO₂-CNT composites is also a function of the TiO₂ particle size. It has been found that when TiO₂ particles are very small (less than 10 nm), they tend to agglomerate around CNT. On the other hand, when particle dimensions are much higher than CNT diameter, TiO₂ particles are rolled up by CNT. An intermediate configuration with a more uniform distribution of TiO₂ particles along CNT walls has appeared to maximize

photocatalytic efficiency of this type of materials. CNT functionalization with oxygen containing groups also plays a crucial role in the photoefficiency of TiO_2 -CNT catalysts by promoting the dispersion of the TiO_2 phase on the CNT surface.

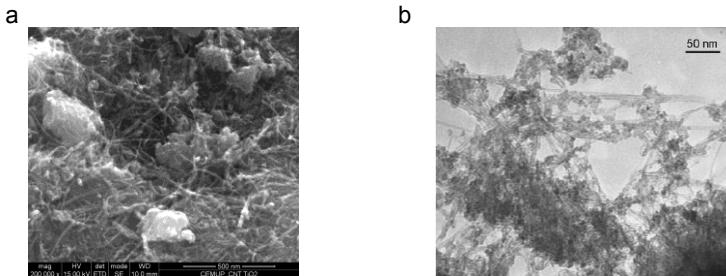


Figure 1. SEM (a) and TEM (b) image of a TiO_2 -CNT composite.

Three different mechanisms are currently being discussed to explain the enhancement of the photocatalytic properties of TiO_2 -CNT composites (Fig. 2) [2,3]: i) a high-energy photon excites an electron from the valence band to the conduction band of anatase TiO_2 and then photogenerated electrons formed in the space-charge regions are transferred into the CNT, and holes remain on the TiO_2 to take part in redox reactions; ii) CNT act as sensitizers and transfer electrons to the conduction band of TiO_2 and then the positively charged nanotubes remove an electron from the valence band of the TiO_2 leaving a hole leading to the formation of hydroxyl radical, which are responsible for the oxidation of several organic compounds; iii) C–O–Ti bond can extend the light absorption to longer wavelengths, similar to what happens to C-doped TiO_2 , thus potentially leading to the improvement of the photocatalytic activity of the composite material.

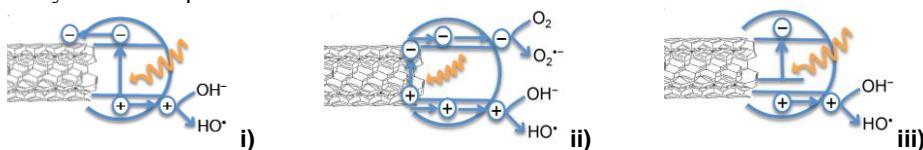


Figure 2. Proposed mechanisms for the CNT-mediated enhancement of the photocatalytic process.

Results on the degradation of different organic pollutants in water are going to be presented using TiO_2 -CNT catalysts as suspensions and immobilized as films [4,5].

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Acknowledgement: Support for this work was provided by FCOMP-01-0124-FEDER-008442 and REEQ/1106/EQU/2005 grants, by LSRE/LCM LA financing program through FCT, and from the European Commission (Clean Water - Grant Agreement Number 227017). CGS and RRNM acknowledge FCT for the scholarships SFRH/BPD/48777/2008 and SFRH/BD/65425/2009, respectively. AMTS acknowledges financial support from POCI/N010/2006.

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OR-4 – Photoisomerisation around a fulvene double bond. Coherent population transfer to the electronic ground state?

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Photoisomerisation around a central fulvene-type double bond is known to proceed through a conical intersection at the perpendicular geometry. The process is studied with an indenyliden-dihydropyridine model compound, allowing the use of visible excitation pulses. Transient absorption shows that *i*) stimulated emission shifts to the red and loses oscillator strength on a 50 fs time scale, *ii*) bleach recovery is highly non-exponential and not affected by solvent viscosity or methyl substitution at the dihydropyridine ring. Quantum-chemical calculations are used to explain *i*) as initial elongation of the central C=C bond with mixing of S₂ and S₁ states. From *ii*) it is concluded that internal conversion S₁ → S₀ does not require torsional motion to the fully perpendicular state. The S₁ population appears to encounter a sink on the torsional coordinate before the conical intersection is reached. Rate equations can not model the observed ground-state recovery adequately. Instead the dynamics are best described with a strongly-damped oscillatory contribution, which could indicate coherent S₁-S₀ population transfer.

Acknowledgement. The Deutsche Forschungsgemeinschaft is gratefully acknowledged for financial support through the Sonderforschungsbereich 450. Financial support from the Spanish Ministry of Education and Science and the European Regional Development Fund (Grant CTQ2007-68057-C02-01/BQU) and the Xunta de Galicia (Grant IN845B-2010/094) are also acknowledged. J.L.P.L. thanks the Spanish Ministry for Science and Innovation (MICINN) for funding by the 2009 "Ramón y Cajal" Program.

ORAL COMMUNICATIONS

OR-5 – Sunscreens as feasible oxygen acceptors in the photo-deoxygenation of heterocyclic N-oxides

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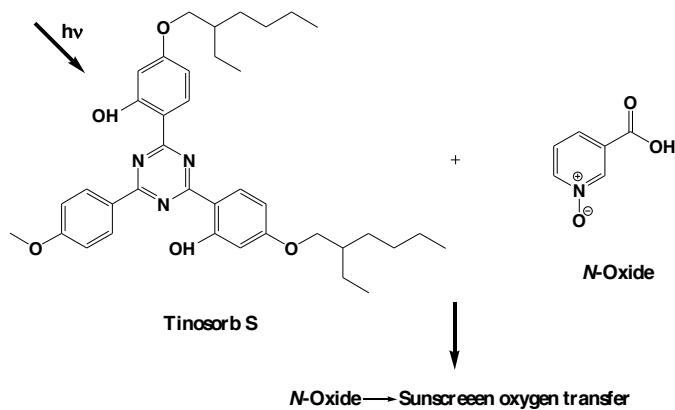
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Photostability is one of the most important properties of an effective sunscreen. Among them, a broadband UV filter, bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S) has been reported as a very photostable UV filter [1]; it efficiently dissipates the accepted energy through intramolecular hydrogen transfer in the excited state followed by internal conversion and thermal deactivation.

On the other hand, heterocyclic N-oxides are biologically active substances. The spectrum of their activity is very broad: it extends from environmentally safe plant growth stimulants and medical agents to exceptionally potent mutagens and carcinogens. It is known that nicotinic acid N-oxide is capable of losing oxygen on heating in the presence of pyridine leading to a simultaneous and quantitative transformation of the latter into pyridine N-oxide [2].

In this context and in the present work, the heterocyclic N-oxide deoxygenation has been studied through the sunscreen excited thermal deactivation. Preliminary results indicate that two very connected processes are taking place: N-oxide deoxygenation and sunscreen oxygenation. Such filter oxidation could be relevant because not only does the degradation of its single components result in a decrease of the UV protection effectiveness but also would be the origin of sensitization processes like phototoxicity and photoallergy [3]. Several photophysical and photochemical techniques have been used in order to determine the mechanism of such processes.

III JORNADAS IBÉRICAS DE FOTOQUÍMICA



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OR-6 – Studies on stimulated emission in dye-doped polymer thin films

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The use of organic wave-guide lasers based on dye-doped polymers has attracted much attention over the last decade for their applications in integrated photonics. The versatility of these systems assures wide tunability (from UV to IR), high efficiency and easiness of production. A major drawback of these devices is their limited operational lifetime, and any realistic application passes for extending it. Dye photodegradation is mainly caused by thermal and/or chemical (photooxidation) processes and different approaches must be followed to overcome them while keeping the desired efficiency in the final device. It is known that an improvement in the polymer thermal conductivity reduces dye thermal degradation due to a more efficient dye-to-polymer heat transfer. On the other hand, photochemical degradation is avoided by using matrices less permeable to oxygen, which is responsible for dye photooxidation.

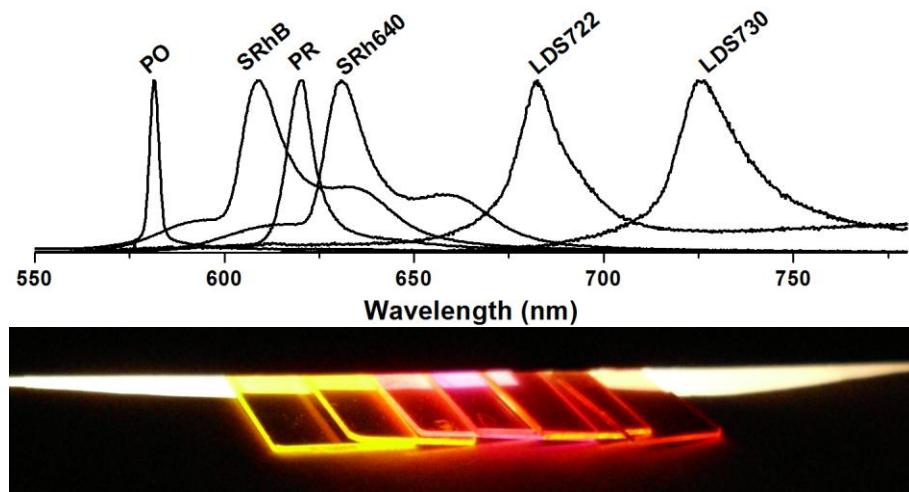


Figure 1. Amplified Spontaneous Emission spectra of Perylene Orange (PO), Perylene Red (PR), Sulforhodamine B (SRhB), Sulforhodamine 640 (SRh640), LDS722 and LDS730. PO and PR are doped in PMMA, whereas the rest of the dyes are in pHEMA. Image below: Picture of waveguides corresponding to the dyes in the spectrum above.

In this contribution we will show the operational optimization of emitting devices based on polymers doped with dyes belonging to the family of perylenes, rhodamines and hemicyanines, covering the spectral range between 550 nm and 730 nm (Fig. 1). Thin films of dye doped polymers are spin coated onto quartz substrates in order to obtain waveguiding structures in which the emitted light is confined into the active film. Two types of devices are obtained depending on the substrate characteristics. For flat substrates there is only waveguiding confinement, and the light is simply amplified when propagating along the film, obtaining at the exit Amplified Spontaneous Emission (ASE). For corrugated substrates, in which a periodic structure has been engraved in their surface, both light confinement and resonant feedback is provided, and Distributed Feedback (DFB) laser emission is excited.

ASE efficiency, gain and photostability measurements are carried out to optimize both the dye concentration and the best polymer matrix for each of the dyes. Once the optimal conditions are known, the DFB laser performance (Fig. 2) of each of the dyes is assessed.

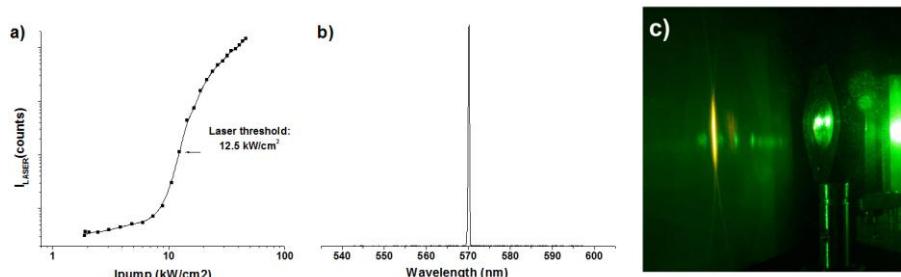


Figure 2. DFB laser performance of PO/PMMA device: a) Laser efficiency curve and laser threshold, b) laser spectrum, and c) emission spot.

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OR-7 – Fluorescence and Laser Performance of Fluorinated BODIPY Dyes

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Fluorine is a unique element for the design of analogs of organic molecules, usually replacing hydrogen at strategic carbon atoms. The very high electronegativity of fluorine, the highest of all the elements, and its relatively small atomic radius have a deep impact on the ensuing molecular properties. The C–F bond is highly polarized, presenting a significant electrostatic component that makes it the strongest bond in organic chemistry. As a consequence, organofluorine molecules usually have higher chemical and thermal stabilities and lower polarizabilities than analogous non-fluorinated molecules, being generally more hydrophobic and more lipophilic [1]. Fluorination also affects the photophysical and photochemical properties of chromophores. Thus, fluorine-substituted chromophores generally show higher photostabilities, with greater resistance to photobleaching and reduced reactivity towards singlet oxygen, enhanced fluorescence quantum yields, and reduced aggregation than their parent non-fluorinated counterparts [2].

Among organic dyes, 4,4-difluoro-4-bora-4a,4a-diaza-5-indacenes, commonly known with the trademarked name BODIPY, are considered today as one of the most useful and versatile fluorophores. The interest in BODIPYs originates from their outstanding photophysical properties, such as high absorption coefficient, high fluorescence quantum yield, high photostability, and low sensitivity to medium effects. Currently, the development of new fluorescent BODIPY dyes has become a booming area of research due to their potential applications [3]. As explained above, fluorination could serve as a general strategy to improve the performance of dyes, but this type of substitution remains almost unexplored in the field of BODIPYs. Very few BODIPY derivatives containing fluorine atoms attached to carbon positions of the boradiazaindacene ring system or its substituents have been described (Figure 1).

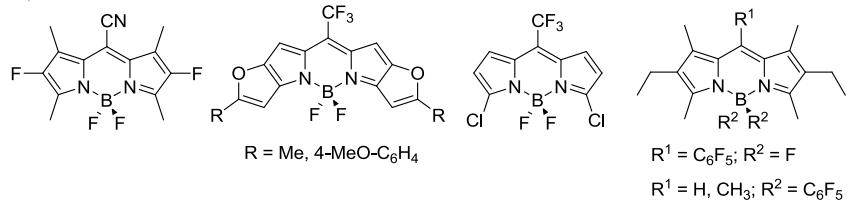


Figure 1

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The first example, 2,6-difluoro-BODIPY, was claimed in a discontinued Japanese patent, although its synthesis has never been reported [4]. More recently, three different research groups have prepared BODIPY derivatives with polyfluorinated substituents at the meso-position or at the boron center [5].

With the final objective of improving the performance of BODIPY dyes for their application in solid-state dye laser materials, we have synthesized a series of new C-fluorinated analogs (Figure 2) and studied their photophysical and laser properties.

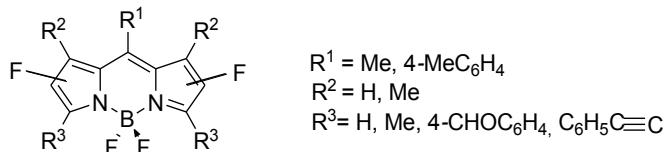


Figure 2

Two general strategies can be followed for the synthesis of new BODIPY derivatives. One is the use of fluorinated pyrroles as starting products, and the other is by post-fluorination of the boradiazaindacene core.

In all cases, the presence of fluorine atoms attached directly to BODIPY core has led to a bathochromic shift of absorption and fluorescent spectral bands, keeping the inherent high fluorescence ability of this dye family, but with improved laser efficiency and photostability.

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OR-8 – Photophysical processes in bicromophoric Naphthalimide-BODIPY systems

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4,4-Difluoro-4-bora-3a,4a-s-indacene (abbreviated as BODIPY) dyes are small molecules that combine strong absorption and relative sharp fluorescence emission peaks with high quantum yields [1]. BODIPY are becoming increasingly popular for their promising applications in numerous fields of modern science and medicine due to their high stability and other desirable photophysical properties and they are therefore often the preferred choice for labelling nucleotides, amino acids and other low molecular weight ligands [2]. However, these compounds also have some undesirable characteristics for many applications in biotechnology. For instant, most show small Stokes' shift ($\Delta\lambda \approx 600 \text{ cm}^{-1}$) which limits their application in cell imaging. When the Stokes' shift of a single dye is insufficient for a particular application, strategies that exploit through-space energy transfer between two dyes (*cassette*) are frequently used [3].

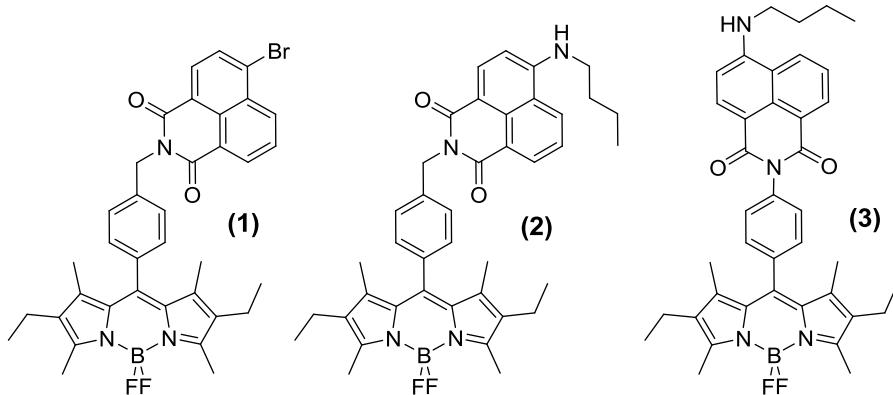


Figure 1. Naphthalimide-bodipy derivatives.

In this communication, a series of newly Naphthalimide-BODIPY cassettes are presented (figure 1). In all cases the BODIPY fragment acts as an acceptor while the Naphthalimide serves as a donor. Absorption, fluorescence and time-resolved fluorescence spectra of the compounds were recorded, and quantum yields for the cassettes excited at the donor λ_{\max} were measured. Excitation in the naphthalimide absorption band did not lead to naphthalimide emission but instead to emission characteristic of the BODIPY core. The

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fluorescence excitation spectrum matches the absorption spectrum, indicating that there is an efficient energy transfer from the naphthalimide to the Bodipy moiety. The quantum yield measurements are consistent with a high efficiency for this transfer.

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ORAL COMMUNICATIONS

OR-9 – Energy transfer from caged Topotecan (a potent anti-cancer drug) to a Rhodamine-cyclodextrin nanocarrier

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Nanocarriers such as cyclodextrins (CDs) have led to intensive studies as they can be used for drug delivery [1]. Moreover, interrogating on the nature of the interactions between drugs and proteins and the time scale of the involved processes is essential for the understanding of the biochemical effects exerted by the drugs inside the human body [2] and their pharmacological importance [3]. In this contribution, we will show results on steady-state and time-resolved picosecond experiments using the anti-cancer drug topotecan (TPT) in solution as well as within a rhodamin-B-substituted β -cyclodextrin (6-monodeoxy-6-mono[(5/6)-rhodamin-B-ylureidol]- β -cyclodextrin, Rh- β CD). The results clearly suggest the existence of an energy transfer process from the initially excited-state donor (TPT in this case) to the acceptor: Rh- β CD.

The typical red emission ($\lambda_{\text{max}} = 583$ nm) of the rhodamin-B, excited in a region where it weakly absorbs ($\lambda_{\text{exc}} = 371$ nm), increases upon addition of TPT (Fig. 1A). The existence of an isoemissive point at ~ 570 nm in Figure 1B points toward a correlation between these emissions and therefore further supports the resonance interaction between both chromophores of the complex TPT:Rh- β CD. We measured the fluorescence lifetimes (ps – ns regime) of TPT in water, in presence of not substituted CD, and interacting with the Rh- β CD structures. We believe that these results are relevant to the fields of drug delivery and nanosensors.

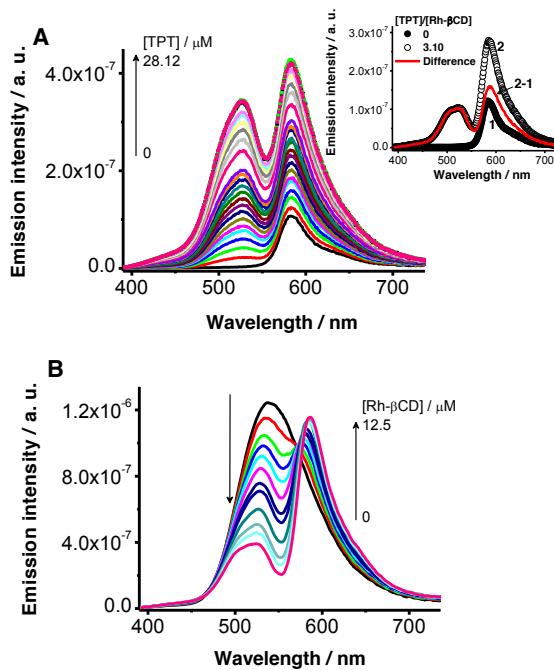


Figure 1. (A) Emission spectra ($\lambda_{\text{exc}} = 371$ nm) of Rh- β CD in water upon addition of different concentrations of TPT (0-28.12 μM). Emission for Rh- β CD by energy transfer is clear evidenced when the contribution of a solution of Rh- β CD in water of the same concentration is subtracted from the whole spectrum, see the inset; (B) Emission spectra ($\lambda_{\text{exc}} = 371$ nm) of TPT in water after subsequent additions of Rh- β CD with water (0-12.5 μM).

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OR-10 – Luminescent polymer nanofibers with high oxygen permeability for photochemical chemical sensing

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Organic polymer nanofibers doped with luminescent ruthenium(II) complexes have been prepared for chemical sensing purposes by means of electrospinning (Figure 1) [1]. Together with common organic polymers used in electrospinning such as poly(vinyl acetate) (PVA) and polystyrene (PS), also more exotic fluorinated ones such as poly(vinylidene difluoride) (PVDF), Teflon AF® or a block copolymer of Nafion®/polyacrylic acid (PAA) have been used. The high O₂ permeability together with the large surface-to-volume ratio of the nanofiber are expected to be key properties for obtaining sensing materials with a fast response and high sensitivity. The low solubility of perfluorinated polymers in common organic solvents together with their low dielectric constant have been found as the main challenges.

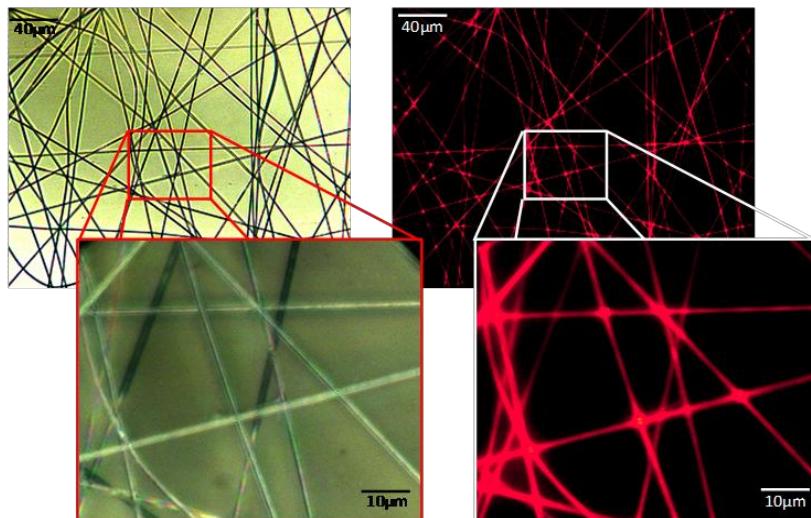


Figure 1. Bright field (left) and luminescence (right) microscopy images of PS nanofibers doped with a ruthenium(II) oxygen indicator dye.

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As far as the luminescent indicator is concerned, three different ruthenium(II) complexes were used: two commercial dyes (tris(2,2'-bipyridine)ruthenium(II) and tris(bathophenanthroline) ruthenium(II)) and a home-made coordination compound, namely tris(5-perfluorooctanamide-1,10-phenanthroline)ruthenium(II). The latter was designed to be directly incorporated into perfluorinated matrices so that, in this way, luminescent Teflon AF® nanofibers have successfully been manufactured by electrospinning for the first time. Capitalizing on their close to diffusion-controlled photoinduced energy transfer quenching of their lowest-lying metal-to-ligand charge transfer (MLCT) triplet excited state [2], luminescent Ru(II) polypyridyls are currently the cornerstone of the marketed last generation dissolved oxygen sensors for water monitoring [3]. They have almost phased out the well established Clark electrode due to the much lower maintenance and resistance to biofouling of the electrolyte-free O₂ sensing terminals [4]. Moreover, by a judicious design of their polyazaheterocyclic chelating ligands, the photochemistry of Ru(II) coordination complexes can be tailored to monitor other environmentally relevant species such as (near neutral) pH [5].

Scanning electron microscopy (SEM) has been used to characterize the morphology and also determine diameter of the manufactured fibers, while fluorescence lifetime imaging microscopy (FLIM) has been applied to study the photophysical properties of the novel nanofibers (Figure 1). A detailed study of the emission decays as a function of the nanofiber parameters and compositions allows extracting valuable information on the presence of different excited species in different microenvironments within the materials. In this way, the polymer nanofibers can be tuned to the target sensing properties. The effect of several parameters such as the luminescent dye structure and concentration, the applied electrospinning potential and deposition time, as well as the distance between the needle and the collector will be presented and discussed in our communication.

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ORAL COMMUNICATIONS

OR-11 – Polyelectrolyte-assisted functionalization of carbon nanotubes with ordered assemblies of a water soluble porphyrin

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The combination of light-harvesting multiporphyrins and all-carbon systems has been pointed out as to provide appealing photofunctional nanomaterials to the development of molecular-scale photonic devices aimed at light-energy conversion [1].

Porphyrins are electronically and sterically tunable by chemical modification on the central metal atom or on the peripheral meso- and/or β -substituents, thus providing a variety of redox potentials and versatile optical properties [2].

Carbon nanotubes (CNTs) can supply an ideal network to promote charge transfer in porphyrin-based systems due to their large carrier mobility and unique transport properties. However, CNTs bundle tightly together over various solvents, in particular single-walled CNTs exist as ropes which are entangled with each other. Non covalent functionalization is an advantageous approach since it fully preserves the electronic network of the nanotubes [3].

In our communication, we present results on the interaction of an hydrosoluble porphyrin – *meso*-tetra(*p*-sulfonatophenyl)porphyrin (TSPP) – with different carbon nanotubes – multi-walled CNTs of different diameter and single-walled CNTs (MWCNT and SWCNT), in aqueous solution at pH 3.

Although pi-pi interaction between the conjugated surface of the CNTs and the aromatic TSPP macrocycle was achieved with the consequent efficient quenching of the porphyrin fluorescence, no ordered supramolecular assembly could be detected.

The addition of polyelectrolytes such as poly(allylamine hydrochloride), PAH, and poly-L-lysine, PLL, helped surpass the solubility problem of CNTs in water by debundling and bringing individual tubes into solution. Furthermore, these positively charged polyelectrolytes facilitated the aggregation of protonated TSPP at the CNTs surface.

J- and H-aggregates of TSPP have been reported earlier which were promoted under specific pH and ionic strength conditions [4]. These type of aggregates are of particular interest in view of their highly ordered molecular arrangement. The acidic conditions of the medium induces the protonation of TSPP pyrrolic nitrogens which imposes the lateral sulfonato groups to adopt a nearly co-planar position relatively to the macrocycle, thus facilitating the interaction with neighbor molecules in a head-to-tail arrangement (J-aggregates). Nonetheless, a co-facial arrangement of TSPP can also be obtained (H-aggregates). In fact, spectroscopic data showed that the nature of the exciton coupling of the transition dipole moment depended on the solution pH, the CNT diameter, and the polyelectrolyte nature (Figure 1A and B).

The assemblies thus formed showed supramolecular chirality and an environmental dependence similar to previous findings [5].

Fluorescence lifetime imaging microscopy (FLIM) was used to spatially map emission lifetimes on the axial dimension of porphyrin - CNT assemblies. The aggregates' morphology and sizes were further investigated upon deposition using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM), Figure 1D.

These novel nanohybrid materials also exhibited excellent optical limiting properties.

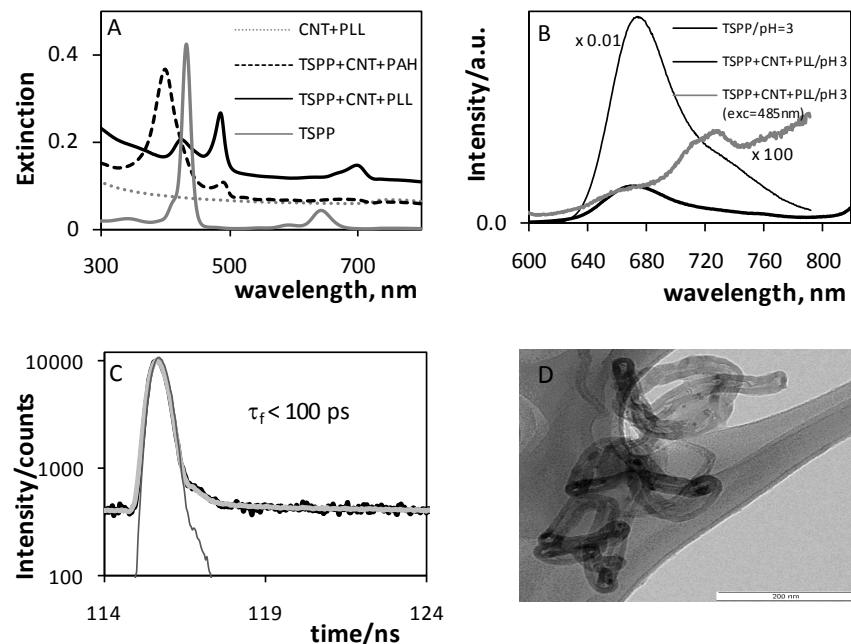


Figure 1. A) UV-Vis and B) fluorescence spectra of diacid TSPP in free aqueous solution and in the presence of MWCNT+polyelectrolytes (pH 3; $\lambda_{\text{exc}}=430 \text{ nm}$); C) Time-resolved fluorescence decay of TSPP in the presence of MWCNT+PLL ($\lambda_{\text{exc}}=485 \text{ nm}$; the thin line represents the instrument response function); D) TEM images of TSPP/MWCNT-PLL system.

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OR-13 – Luminescent Silica Nanoparticles Engineered for Enrofloxacin Sensing based on FRET

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Enrofloxacin is a broad spectrum antibiotic of the fluoroquinolone family, widely used in human and veterinary medicine. Its widespread use causes contamination of aquatic systems, potentially triggering the appearance of antibiotic-resistant bacterial strains. Consequently, the development of quick and cheap tests for detecting the presence of this target analyte would be of great interest. Methods based on optical indicator dyes are usually affordable, sensitive and user-friendly. In this work, we have explored a new photochemical method for optical detection of enrofloxacin in water based on tailor-made luminescent silica nanoparticles together with a FRET (*Förster Resonance Energy Transfer*) signalling mechanism. Since the efficiency of FRET depends on the distance between two chromophores, –a luminescent FRET donor (**D**) and a suitable acceptor molecule (**A**)–, changes on a FRET process can be employed to signal the binding of two species labelled with appropriate **D-A** pairs. These **D-A** pairs must meet the condition of a good spectral overlap between **D_{em}** and **A_{abs}**, making possible the energy transfer from the excited **D** to ground state **A**. Concerning selective analyte recognition, our group has a vast experience on the development of *biomimetic* receptors based on molecularly imprinted polymers (MIPs) [1] and has demonstrated the success of these “*plastic antibodies*” for waterborne fluoroquinolones determination by HPLC [2].

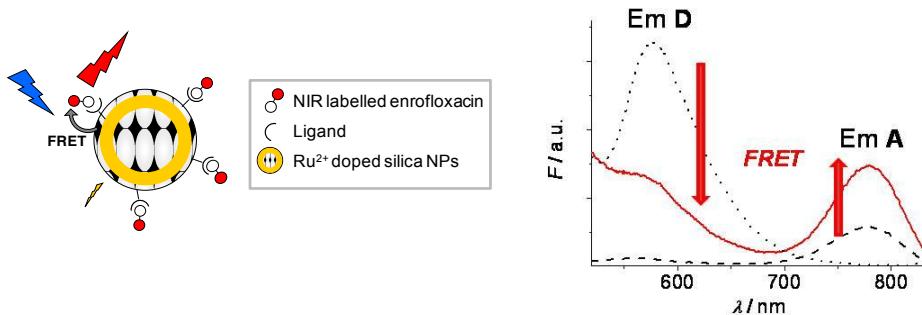


Figure 1. Schematic representation of the novel nanoparticle (NP)-based Ru(II)-cyanine FRET system described herein. Upon binding of the NIR dye-labelled enrofloxacin to the luminescent NPs surface (*left*), the energy of the excited $\text{Ru}(\text{bpy})_3^{2+}$ complex is transferred to the ground state cyanine fluorophore. As a consequence, the Ru(II) emission is quenched and the NIR emission of the organic fluorophore at 800 nm is enhanced (*right*).

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For the FRET system, we have chosen a cyanine-labelled enrofloxacin, with $\lambda_{\text{abs}}/\lambda_{\text{em}} = 705/793$ nm and $\tau_F = 0.92$ ns, as the FRET acceptor, and the Ru(bpy)₃²⁺ complex (bpy: 2,2'-bipyridine), with $\lambda_{\text{abs}}/\lambda_{\text{em}} = 450/584$ nm and $\tau_L = 0.40$ μ s, as the FRET donor. Besides the detection in the NIR window, –enabled by the cyanine label–, an advantage of this **D-A** pair is the long emission lifetime of the Ru(II) complex (even in the presence of air). This feature allows a facile discrimination of the actual FRET-sensitized cyanine emission at 800 nm, from that arising from the direct excitation of the unbound cyanine. In order to maximize the signal output [3] and for minimizing the Ru(II) luminescence quenching by dissolved oxygen [4], the FRET donor molecules are encapsulated into silica nanoparticles (NPs) of ca. 150 nm diameter. Since such NPs are rather large in comparison with the FRET scale (FRET occurs normally within $1 < d_{\text{D,A}} < 10$ nm) [5], it is convenient to have the maximum amount of **D** luminophores located on the external shell of the NPs. Interestingly enough, the distribution of Ru(II) complexes can be controlled at will by selecting the time at which the Ru(bpy)₃²⁺ dye is added during the Stöber synthesis of the silica NPs [6]. Here we will show how the procedure followed for NPs doping with the Ru(II) dye affects the FRET efficiency on assays performed with the luminescent NPs and the NIR-labelled enrofloxacin. Finally, and in order to confer recognition abilities to the NPs, nanometric MIP shells, molecularly imprinted with our target analyte (enrofloxacin), are grown around the silica NP core, providing selective binding points for the fluoroquinolone. The aim is that the multifunctional core-shell nanoparticles could then be employed for competitive/displacement assays [1] using FRET signalling in the optical NIR window. This contribution will mainly focus on optimization of the photochemical FRET process and the spectroscopic characterization of both the NIR label and the luminescent nanoparticles.

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OR-14 – Quantum Dot as photoluminescence lifetime-based nanosensors

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Semiconductor nanocrystals, namely, quantum dots (QDs), present a set of unique photoluminescence properties, which has led to increased interest in using them as advantageous alternatives to conventional organic dyes [1,2]. Many applications of QDs involve surface modification to enhance the solubility or biocompatibility of the QDs. One of the least exploited properties of QDs is the very long photoluminescence lifetime [3,4], which made them highly sensitive and selective, since they can be easily distinguished from other interfering short-lived fluorescence, such as cell autofluorescence.

Because the photoluminescence of QDs arises from the recombination of the exciton, all changes in charge or composition on the surface and environment of QDs could affect the efficiency of core electron-hole recombination and consequently the luminescence efficiency, fluorescence decays and dynamics. On these grounds, we show the effect of surface modification on fluorescence properties of QDs of different sizes, especially focusing on changes on fluorescence lifetimes. In this work we explore the potential of time-resolved fluorescence measurements for the detection of specific processes that alter QD emission [5]. We survey representative sensing examples based on different interaction mechanisms between QDs and other species, such as organic fluorophores or fluorescent proteins, by means of electrostatic interactions, charge transfer, or energy transfer.

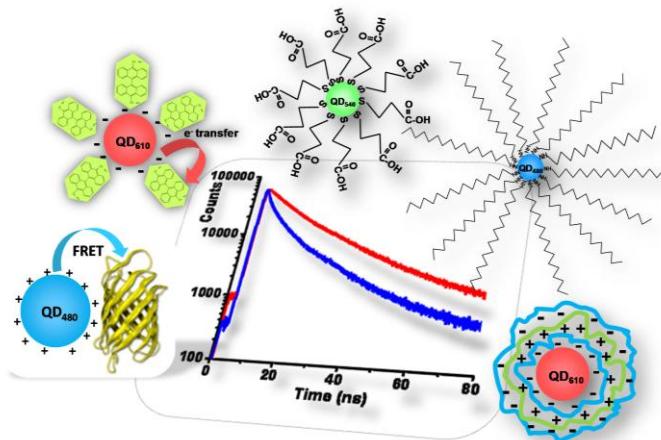


Figure 1. Different surface modifications of QD nanoparticles which produce changes in the photoluminescence lifetime.

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In particular, from all these examples, two systems were investigated in depth for the development of the two first CdSe/ZnS QD photoluminescence lifetime-based pH and Cl^- nanosensors. On one hand, in the pH-nanosensor, the average lifetime of mercaptopropionic acid-capped QD (QD-MPA) showed a linear response in the pH range of 5.2-6.9, what suggests potential application for pH determination in physiological samples, such as endosomes and lysosomes ($\text{pH} = 5\text{-}6.5$), or for the detection of some tumor cells ($\text{pH} = 6.4\text{-}6.9$). In this system, the responsible for the changes in the PL lifetime with pH was the protonation/deprotonation of the MPA carboxylic acid affecting the surface of QD-MPA [6].

On the other hand, the Cl^- -nanosensor takes the advantage of the response towards Cl^- of a different indicator, lucigenin. Lucigenin can be coupled to QD-MPA through electrostatic interaction between negatively charged MPA on QD surface and the positively charged nitrogens of the acridinium derivative (QD-Luc) [7]. The immobilisation of lucigenin on the surface of QD-MPA caused a quenching in the nanocrystal photoluminescence, and therefore a decrease in the photoluminescence lifetime, by means of electron transfer from the QD conduction band to the acridinium derivative. However, an increase in the average lifetime of QD-Luc conjugates was detected upon addition of Cl^- , as a result of the interruption of the charge transfer quenching mechanism between QD and lucigenin.

The proposed QD-MPA and QD-Luc nanosensors have been satisfactorily applied for the determination of Cl^- or pH estimation, respectively, in simulated intracellular media, with high sensitivity and high selectivity toward most of the intracellular components.

The results obtained demonstrate that time-resolved fluorescence is a useful tool for QD-based sensing to set the basis for the development of time-resolved-based nanosensors. The excellent photophysical properties of QDs together with the typical advantages of time-resolved fluorescence overcome most of the limitations of the use of organic chromophores and steady state fluorescence as analytical signal, such as variations in the observation pathlength and probe concentration, light scattering, and photobleaching. We provide an overview of the potential of this technique that will help to set a basis for the use of modified QDs in fluorescence lifetime-based applications such as Fluorescence Lifetime Imaging (FLIM).

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ORAL COMMUNICATIONS

OR-15 – Methodology to obtain highly fluorescent organic- and water-soluble CdSe/ZnS core-shell quantum dots capped with thiols

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Core-shell CdSe/ZnS quantum dots (QDs) are highly fluorescent systems compared with organic dyes and are passivated with organic ligands to allow them to remain stable as colloidal solutions in organic solvent (for optoelectronic applications) or water (for biological applications). Trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO), as well as fatty amines, are the most common ligands used in the synthesis of QDs [1].

Thiolate ligands can replace TOPO and amine ligands and thus bind to the surface of CdSe/ZnS QDs more strongly, but such exchange produces QDs with drastically diminished Φ_F (more than 50%) [2]. This has been explained as being due to a spontaneous binding of thiolates to the ZnS surface, causing a significant alteration [3].

We report that the ligand replacement of amine of commercial highly fluorescent CdSe/ZnS core-shell QDs by thiol in the thiolate form can even improve their emission performance if the thiolate is generated close to the QD surface assisted by the amine ligand. This strategy was applied to the preparation of highly fluorescent organic- and water-soluble QDs that exhibited a higher photostability than the initial amine-capped QDs.

In order to demonstrate the generality of this methodology, commercial QDs from different suppliers as well as home-made QDs were used. All of them showed a similar behavior, indicating the amine ligands play a key role in the functionalization process. Nuclear magnetic resonance (¹H-NMR), fluorescence, and X-ray photoelectron (XPS) spectroscopies were used to demonstrate that the attachment of thiol ligands to lead to either organic-soluble or water-soluble QDs can be performed under mild conditions preserving, or even enhancing, not only the emission properties of the nanoparticles but also their photostability.

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OR-16 – Association Dynamics of DNA Minor Groove Binders

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The recognition of specific DNA sequences has an enormous diagnostic and clinical potential because of the genetic origin of many pathologies, and the influence of particular genotypes in the response to medical treatments. We have recently developed synthetically easily accessible aza-bisbenzamidines which bind and sense specific doublestranded DNA (dsDNA) featuring AT rich sites [1]. Very few is known about the underlying mechanism of the binding and the structural properties governing the binding affinity and specificity. Fluorescence Correlation Spectroscopy (FCS) gives access to the very fast binding dynamics and yields crucial information for a better understanding of the binding process [2,3].

We present results for the binder bisbenzamidine labeled with Oregon Green488 and different dsDNA sequences (AAATT, AATT and GGCCC).

The fluorescence emission of this binder increases strongly in the presence of DNA which allows us to obtain the rate constants of association and dissociation by FCS. The association rate constants (k_+) are significantly lower than the diffusion-limited rate constant and depend strongly on the specific DNA sequence. On the contrary, the dissociation rate constant (k_-) is much less sequence specific.

Surprisingly, the specific interactions which stabilize the binder in the minor groove of the DNA are not very different among different sequences, but the sequence specificity is mainly determined by different geometric and orientational conditions during the association process.

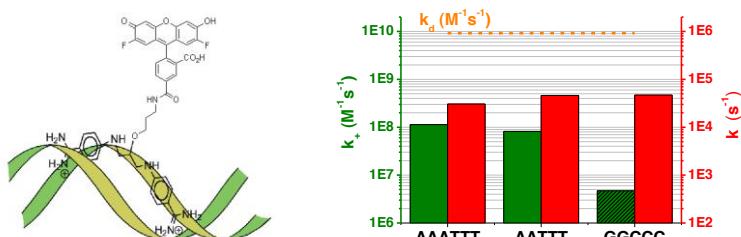


Figure 1. Scheme of the binder (left) and rate constants of association and dissociation (right).

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OR-17 – Gold nanoparticles functionalised with PET-based fluorescent probes for intracellular measurements of pH

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Protons are one of the most important intracellular species of interest. For instance, the pH in tumour cells has been shown to be abnormal [1] and elevated lysosomal pH has been detected in neurodegenerative disorders of childhood [2]. Photoinduced electron transfer (PET) processes are one of the mechanisms operating in many fluorescent probes. PET fluorescent sensors have been widely described as useful for the detection of cations and anions of interest such as, protons, calcium and fluoride. The intracellular imaging of pH with PET-based fluorescent sensors is extensively used for studies of the biochemical machinery of cells or as a diagnostic tool in medicine [3]. With our work, we want to improve the signalling of acidic organelles within cells. To do so, we have designed and synthesised a PET-based pH probe and we have conjugated the pH probe to a gold nanoparticle of 2-3 nm size.

The first aim of this research was to synthesise the PET nanoprobes and then to study whether the PET process operating in the free ligand (ON-OFF switching of fluorescence triggered by pH) takes also place when the PET-based pH probe is bound to the surface of the gold nanoparticle. The second aim of our work was to use the synthesised PET-based nanoprobes for imaging acidic environments within Chinese hamster ovary (CHO) cells.

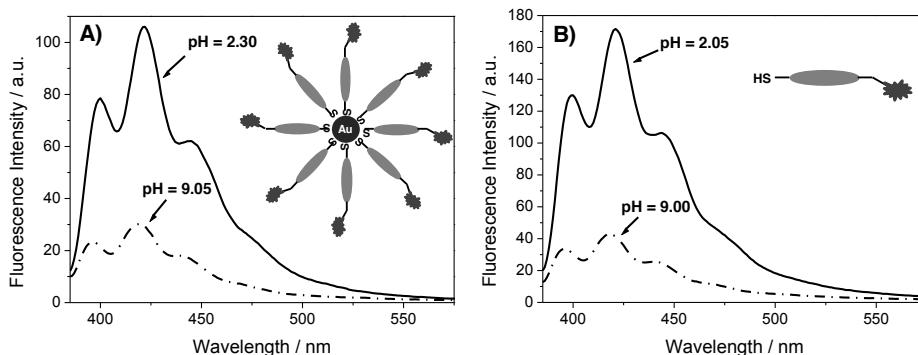


Figure 1. Fluorescence emission spectra of **A)** PET nanoprobe and **B)** PET-based pH probe at different values of pH, **basic pH** (--) and **acid pH** (—). $\lambda_{\text{exc}} = 370 \text{ nm}$.

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In order to achieve the aims of our research, the synthesis of a PET-based pH probe incorporating a thiolated moiety was carried out. The ligand was unambiguously characterised by means of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, MS, FT-IR, UV-vis, steady state fluorescence and time resolved fluorescence. The PET pH probe was then used to decorate the surface of gold nanoparticles. The final PET nanoprobe was characterised by means of $^1\text{H-NMR}$, TEM, FT-IR, UV-Vis, steady state fluorescence and time resolved fluorescence. The fluorescence emission of the PET-based nanoprobe was recorded in acidic and basic media. The emission of the PET nanoprobe was quenched in alkaline media and enhanced in an acidic environment (Fig. 1A). The free ligand was studied under the same conditions affording, as expected, a similar ON-OFF switching process (Fig. 1B). The PET-based nanoprobes were used for intracellular imaging of acidic environments in CHO cells by confocal fluorescence microscopy. Acidic organelles within the cells⁴ are known to have a pH of ~ 4 – 5. The fluorescence of the PET nanoprobe was turned-on when located in the acidic organelles of the CHO cells. From these results it can be deduced that the PET nanoprobe were signalling the acidic regions within the intracellular environment of CHO cells and hence are potentially useful probes for bioimaging of acidic organelles and pathologies associated to unbalanced pH of such cellular structures.

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OR-18 – Study of the Fluorescence Enhancement of Stable Core-Shell Silica Nanoparticles Using Single Molecule Emission Spectroscopy

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Recently, we used single molecule spectroscopy to map the distribution of individual chromophores interacting with silica-based nanomaterials [1, 2]. Here, we present our results from ensemble average and single molecule spectroscopy studies on the fluorescence enhancement mechanism of DY-630-maleimide covalently incorporated into two different sized core-shell silica nanoparticles. Single molecule experiments (Figure 1A) show increased photobleaching stability and a 10-fold increase in the lifetimes upon encapsulation, in agreement with the ensemble average experiments. The interaction with the rigid environment of the core-shell nanoparticles is the main reason for the enhancement in photostability and quantum efficiency of the encapsulated dye. Polarization and photon antibunching studies of the behavior of single silica core-shell nanoparticles suggest the possibility of dye-dye interactions, such as energy hopping (Figure 1B) and singlet-singlet annihilation (Figure 1B) that limit the fluorescence enhancement and can explain the higher fluorescent enhancement of the 30 nm particles (~20 times) with comparison to the 15 nm ones (~ 15 times).

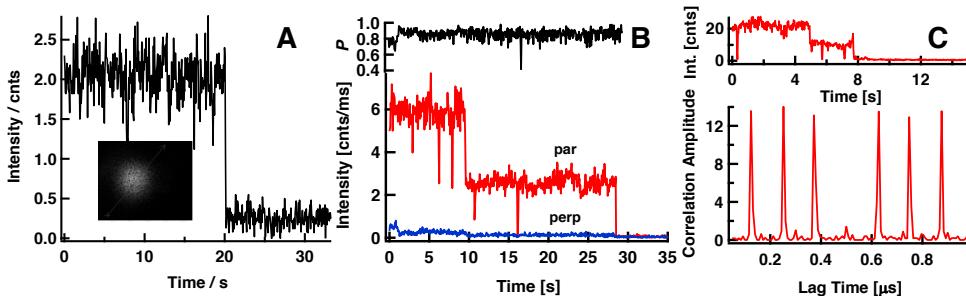


Figure 1. A) representative photobleach trace of single DY-630-maleimide nanoparticle complex; B) example of $I_{||}$ and I_{\perp} -polarized fluorescence traces (bottom pannel) along with the calculated polarization trajectory (top pannel) corresponding to emission from multiple DY-630-MI chromophores and energy hopping in the multichromophoric system; C) Typical intensity trace (top pannel) and interphoton arrival-time distribution (bottom pannel) recorded for the 15 nm size nanoparticle demonstrating efficient S-S annihilation in individual multichromophoric nanoparticle.

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OR-19 – New magnetic-luminescent nanoparticles composed by ferritin with linked phycocyanins and phycoerythrins

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Ferritin, the molecule that stores iron in biological systems, is one of the most paradigmatic biomaterials because of its iron biominerization process, which has inspired the use of its cavity to produce a number of biomimetic ferritins reconstituted with non-native inorganic materials [1]. In other hand, biliproteins are a family of proteins from microalgae, being the main molecules: allophycocyanin (APC), C-phycocyanin (C-PC) and B-phycoerythrin (B-PE) [2]. Due to their high fluorescence efficiency and their intense colours, these proteins have been used widely: in fluoro-inmunoassays, in FRET assays with commercially available antibodies, in flow cytometry and in single-molecule imaging techniques for identifying in free solutions molecules with potential for use in high-speed detection of specific disease markers [3].

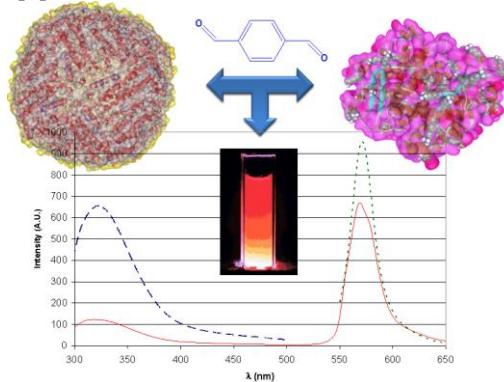


Figure 1. Fluorescence emission spectra of ferritin (---), B-PE (---) and Fer-BPE (—) nanoparticle.

Actually nanotechnology grows continuously and could be defined like the engineering of functional systems at the molecular scale. So, one of the main challenges in this area is to build multifunctionality in a nanostructure and in this context, magnetic nanoparticles have been suggested for a great number of applications as new magnetic devices (data storage, carriers for bioseparation, labeling of cells and contrast-enhancing media). Incorporation of luminescent functionality to magnetic nanoparticles is of considerable value in numerous areas, especially in the biomedical one. So, the coexistence of these two properties make possible the *in situ* detection and monitoring by fluorescence imaging of the nanoparticles movement under and external magnetic field, which could be of a enormous interest both

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from therapeutic and diagnostic point of view. In spite of this interest, there are few examples of magnetic-fluorescent nanoparticles and for this reason, we have built bioconjugates using ferritin and biliproteins and these have been characterized using uv-visible absorption spectroscopy and fluorescence spectroscopy (steady-state emission and anisotropy).

Highly pure biliproteins were obtained by our group from different microalgae using a methodology based en expanded bed adsorption chromatography [4]. Ferritin was purchased from Sigma Chemicals (USA). In the preparation of the ferritin-biliproteins (Fer-bili) nanoparticles, same molarities of both proteins were dissolved in phosphate buffer (pH 7.0). Then, a tereftaldehyde solution was added drop-wise to Fer-bili solution (Figure 1). The reaction was allowed to proceed and the solution was then dialyzed against phosphate buffer overnight. After dialysis the protein reaction mixture was applied to a Sephadex-300 column. Individual proteins and Fer-bili nanoparticles fractions were eluted with the same buffer and characterized spectroscopically.

Table 1: Spectroscopic parameters from ferritin-biliproteins luminescent nanoparticles

Luminescent nanoparticle	Absorbance Maxima (nm)	Fluorescence Maxima (nm)	Fluorescence Signal colour
Ferritin-APC	280, 650	656	Red
Ferritin-CPC	280, 620	634	Orange
Ferritin-BPE	280, 545, 565	572	Yellow

We have made use of the lysine residues located at the external ferritin shell and biliproteins were covalently joined to the ferritin by reaction of their amino groups. A mixture of biliprotein and ferritin in the same ratio as in the conjugate was used as control. The conjugate was characterized by the absorption and emission properties, which were compared with those of the separated proteins and the control. In the uv-visible region, the absorption spectrum of the conjugate was a sum of the contributions of the biliprotein and the ferritin.

The nanoparticles showed two fluorescence emission peaks, one attributed to ferritin and the other attributed to biliprotein. However, the control had only a single fluorescence emission peak from biliprotein. Furthermore, although the conjugate contained the same quantity of biliprotein as the control, the emission peak in the conjugate is far lower than of the control, which suggested that the excited energy can be transferred from the ferritin to the biliprotein in the conjugate, but not in the control. In general, fluorescence spectra of biliproteins are modulated by fluorescence resonance energy transfer (FRET) between the chromophores that they have, therefore when we construct the biological nanoparticle using biliprotein and ferritin energy transfer must decreases and an increase in the anisotropy spectra must be observed. We have built three bifunctional nanoparticles that present different optical properties (Table 1).

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OR-20 – Light-activated biomimetic molecular switches

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A molecular switch is generally described as a molecular device that can be reversibly interconverted between two different states, by means of an external stimulus [1]. Within the different kinds of excitation sources that are available, photochemical energy presents multiple advantages. For example, light energy can easily produce photoinduced *cis-trans* isomerizations of N=N and C=C double bonds. As switches based on azobenzene (with N=N double bonds) have been already widely studied, the design and synthesis of other molecular switches different in size, polarity and photoisomerization mechanism is considered an attractive research target [2].

Therefore, the *cis-trans* isomerization of C=C double bonds distinguished in the chromophore of the protonated Schiff base of retinal (PSB-retinal) during the process of vision was considered [3,4]. For the past few years in our research group different prototypes of molecular switches with chemical structures based on the PSB-retinal have been studied thoroughly [5,6]. Here we present the photochemical and photophysical study of new prototypes, different from those previously characterized, whose chemical structure is shown in **Figure 1a**.

In order to compare the results of the study of molecular switches based on the PSB-retinal, we also performed the study of other prototypes of molecular switches based on the green fluorescent protein (GFP) chromophore [7], which also undergo *cis-trans* isomerizations of C=C double bonds. The basic structure of the switches based on the GFP chromophore is shown in **Figure 1b**.

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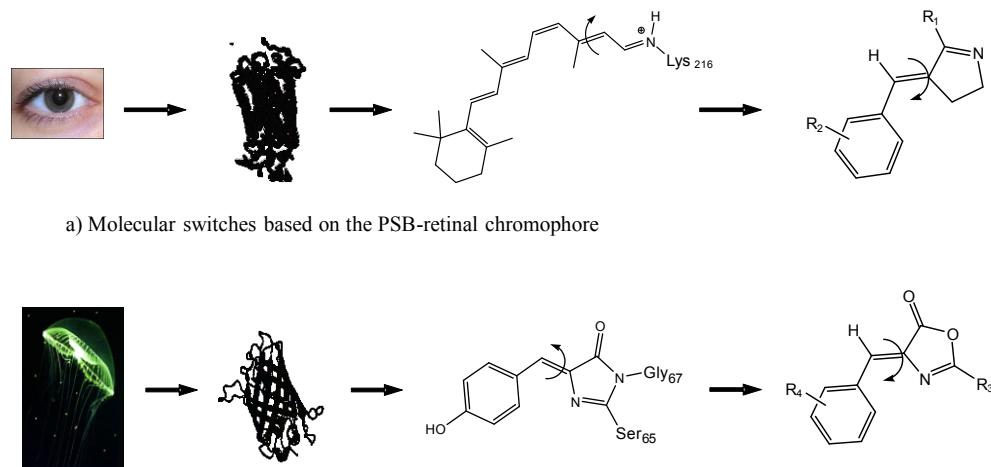


Figure 1.

Our future goal is the achievement of optical control of the structure and function of more complex structures linked to the molecular switch by using light energy.

In this communication the influence of the solvent, irradiation wavelength, cauterization of the nitrogen and substituents presents in the molecular switches in the isomerization process will be discussed.

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ORAL COMMUNICATIONS

OR-21 – Molecular logic switching with spiropyran-fluorophore dyads

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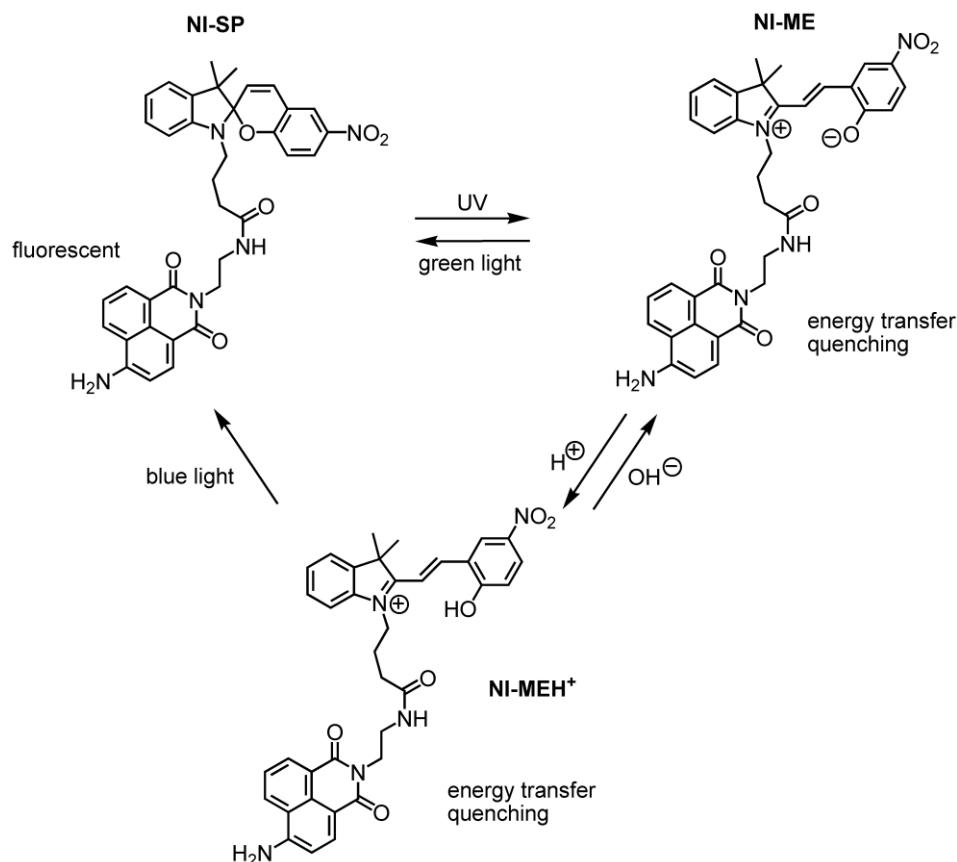
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Photochromic compounds have been recently shown to be of interest for the realization of molecular fluorescent switches [1]. Among the classical types of organic photochromes spiropyrans are of special interest because they involve three different states: the ring-closed spiro form (SP), the unprotonated merocyanine form (ME), and the protonated merocyanine form (MEH^+). The former two (SP and ME) are related through the photochromic process, while the latter two (ME and MEH^+) are in an acid-base relationship (Scheme 1). Hence, the different forms of spiropyran photochromes can be interconverted by the application of light inputs (UV and visible light) and chemical inputs (protons, base). When integrated in dyads with covalently linked fluorophores, the different forms of the photochrome can show differentiated excited state communication with the fluorophore unit. This can be often resumed by photoinduced electron transfer and electronic energy transfer quenching pathways (Scheme 1). Careful photophysical design enables fluorescence switching, as will be shown in this presentation [2]. The binary nature of the switching (implication of ON and OFF states) can be interpreted in terms of molecular logic, which has recently attracted much interest for the design of smart molecular materials for information processing [3,4]. In detail, comprehensive logic functions like reversible logic [5] and sequential logic have been realized [6]. For example, the sequential logic device behaves as a molecular keypad lock, *i.e.*, the fluorescence signal as output of the device is only observed if a particular sequence of input signals (chemical, optical) is applied in the right order.

The synthesis and photophysical/photochemical characterization of the novel dyads will be discussed. This includes details about the photochromic process, time-resolved fluorescence, and estimation of energy transfer key parameters. Furthermore, it will be outlined how the design of the molecular entities led to advanced functionality in form of logic devices.



Scheme 1. Interconversion of spiropyran forms and energy transfer quenching of fluorescence.

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ORAL COMMUNICATIONS

OR-22 – Halogenated BODIPY as generators of singlet oxygen

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The first reports about Boron DiPyrromethene fluorophores (BODIPY) date from the sixties, but it was not until the nineties when they called the attention of the scientific community [1]. Since then, the number of publications claimed their excellent photophysical and lasing properties has growth exponentially. Typically BODIPY are characterized by strong absorption and fluorescence bands in the visible with nearly negligible triplet state absorption [2]. This feature together with their photo, chemical and thermal stability explain why BODIPY are actually the most used active media in tunable dye lasers, even in the solid state [3]. In the last decades many efforts are being done trying to span the application fields (mainly in biomedicine) of these fluorophores (i.e. acting as sensors or markers in biochemical systems) [2c,3].

In this sense another alternative would be to populate the triplet state of BODIPYs. The high fluorescence ability of BODIPYs is in part due to the low probability of intersystem crossing. However, in photodynamic therapy efficient and stable photosensitizers are required to produce singlet oxygen and in this way destroy tumor cells. It is widely known that the formation of single oxygen can be accomplished via the population of the triplet state upon excitation of an appropriate fluorophore. This aim can be achieved in BODIPYs adding halogen by the so called heavy atom effect [4]. In this way, the intersystem crossing probability greatly increase and also the triplet state population, which otherwise is nearly empty.

In the present work we report three series of iodinated BODIPYs. The synthetic method allows obtaining mono, di, tri or tetraiodinated derivatives controlling also the position in which they are anchored. We should emphasize that these are the first examples of BODIPY dyes with more than two halogens in the BODIPY core. Quantum mechanic simulations of the electronic charge distribution and electrostatic potential of the BODIPY derivatives predict those chromophoric positions more suitable to the electrophilic attack by the iodine atom (considering also steric reasons), thus, explaining the experimentally observed regioselectivity in the iodination. Figure 1 shows as an example a series of studied BODIPYs.

On the other hand, the photophysical properties of all the iodinated BODIPY derivatives were recorded and analyzed in detail. As expected the photophysics of these compounds are controlled by the heavy atom effect since the fluorescence emission drastically decrease due to intersystem crossing. Indeed, the higher the number of iodine atoms the larger the decrease of the fluorescence efficiency. Nonetheless, this trend was not true in all the

chromophoric positions where the iodine is attached. In fact, the presence of iodine at the end and/or beginning of the delocalized π system (3 and 5 positions) is beneficial for the fluorescence emission, contrary to what was expected for halogens (Figure 2). Such effect was explained in terms of the push-pull effect which favours the delocalization of the π system counteracting the heavy atom effect. Theoretical simulation of the electronic charge distribution confirms the higher aromaticity of the chromophore upon substitution at 3 and 5 positions.

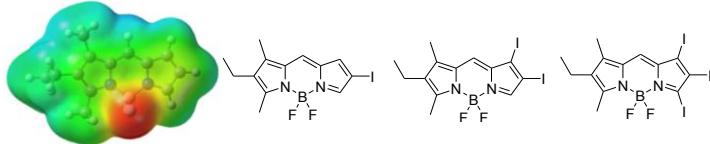


Figure 1. Molecular structure of one group of iodinated BODIPY, together with the potential electrostatic mapped onto the electronic density for the reference compound.

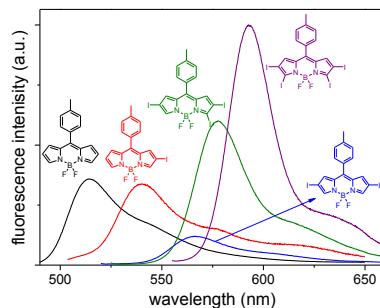


Figure 2. Fluorescence spectra (scaled by their fluorescence ability) of the iodinated derivatives of 8-tolyl BODIPY.

The population of the BODIPY triplet state is corroborating by singlet oxygen generation measurements. Indeed, present iodinates BODIPYs shows singlet oxygen generation quantum yields even higher than compounds recognized as efficient photosensitizers (rose bengal). Therefore, the obtained iodinated BODIPY derivatives are promised agents to be employed in photodynamic therapy.

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OR-23 – New 8-amino-BODIPY derivatives: surpassing laser dyes at blue-edge wavelengths

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The synthesis and development of efficient blue light emitting materials and devices is a driving force in the search for new highly-efficient and photostable blue laser dyes, whose applications would go beyond data storage and displays [1]. Blue laser dyes would be especially important in chemical and biological research and should have an impact in applications such as microscopy, underwater communications, remote sensing and photo/electroluminescent devices [2].

Here, we report the design, synthesis and characterization of new tailor-made BODIPY dyes with efficient absorption and emission in the blue-spectral region.

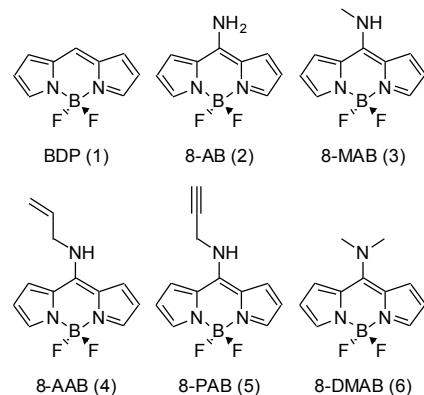


Figure 1. Molecular structure of the new 8-amino substituted BODIPY dyes.

The major challenge is the effective management of the electron donor strength of the substitution pattern to modulate the emission of these novel dyes over a wide spectral range (435-510 nm). A direct relationship between the electron donor character of the substituent and the extension of the spectral hypsochromic shift is stated through the energy raise of the LUMO state. However, when the electron donor character of the substituent is high enough,

an intramolecular charge transfer process appears to decrease the fluorescence ability of these dyes, mainly in polar media. Some of the reported novel BODIPY dyes provide very high fluorescence quantum yields, close to the unit, and large Stokes shift, leading to highly efficient tunable dye lasers in the blue part of the spectrum, which up to now remains an unexploited region with BODIPYs. In fact, under demanding transversal pumping conditions, the new dyes lase with unexpectedly high lasing efficiencies, of up to 63%, with high photostabilities, outperforming the laser action of other dyes considered as benchmarks in the same spectral region.

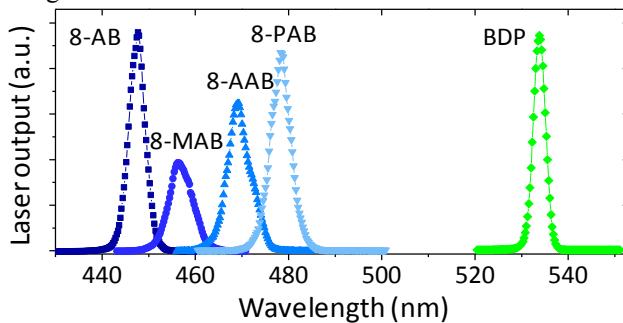


Figure 2. Lasing emission spectra of the new 8-amino substituted BODIPY dyes transversally pumped at a wavelength near their absorption maxima (400 nm). The intensity of the emission bands is related to the lasing efficiency of each dye. For comparison purpose the corresponding data to the fully unsubstituted BDP dye pumped at 500 nm under otherwise identical experimental conditions are included.

Considering the easy synthetic protocol and the wide variety of possible substituents, we are confident that this strategy could be successfully extended to development of efficient blue-edge emitting materials and devices impelling biophotonic and optoelectronic applications.

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OR-24 – Photophysics of Ionic Liquids

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Ionic liquids are a class of organic salts with a melting point below 100°C. They are considered green alternatives to organic solvents as reaction media due to their low volatility, high thermal stability and high ionic conductivity. Luminescence in ionic liquids was mostly studied by dissolution of selected fluorescent compounds with the goal of understanding some properties of ionic liquids [1]. Some studies with imidazolium ionic liquids showed the presence of luminescence from the neat ionic liquid, but it was proved that it comes mostly from impurities [2]. True intrinsic luminescence arises from ionic liquids with lanthanide complexes as one of the anions [3]. Active pharmaceutical ingredients (API) in an ionic liquid form may also be synthesized, and many of them also display intrinsic luminescence.

This communication describes the photophysics of two distinct luminescent ionic liquids. As a first example, an intrinsic luminescent ionic liquid based on europium(III) tetrakis(β -diketonate) complex with a tetraalkylphosphonium as counterion was synthesized. This compound was characterized by several techniques, including differential scanning calorimetry and NMR, showing it can be a supercooled ionic liquid at room temperature. Photophysical characterization displays the antenna effect, enhancing the europium luminescence. The intensity of the europium luminescence is quenched by temperature, and its luminescence decay is non-exponential, which is explained by homoatomic energy transfer between equivalent europium ions.

The second example is an ionic liquid consisting of choline (cation) and naproxen (anion). The naproxen photophysics was studied using UV/Vis absorption and fluorescence spectroscopy. Naproxen aggregates (dimers) were identified in these measurements, and their formation is temperature dependent, being favoured at lower temperatures. Fluorescence decays display the formation of dimers and possibly excimers (excited-state dimers). These results demonstrate that at the microscopic level the naproxen anions tend to aggregate at lower temperatures, affecting its interactions with light.

The connection between these measurements and the ionic liquid structure will be made, as well as its implications in terms of light stability and macroscopic physical properties such as viscosity.

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OR-25 – *Non-vertical* Triplet-Triplet Energy Transfer in condensed phase: definition and quantification of the reaction coordinate.

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A large number of natural and artificial photoreactions take place through the participation of triplet-states, due to the long lifetime and high reactivity of this species. However, due to the extremely low absorption coefficient of the $T_n \leftarrow S_0$ transitions in organic molecules, direct excitation to the triplet state is rarely observed. Thus, population of the triplet state takes place either by intramolecular intersystem crossing from an excited singlet state or by *intermolecular* energy transfer from a sensitizer donor triplet to an acceptor singlet state. The last process, known as Triplet-Triplet energy transfer (TET), was first described by Terenin and Ermolaev in their seminal study of the sensitized phosphorescence of frozen solutions of aromatic molecules [1]. TET is explained by an electron exchange-resonance mechanism [2], according to which the excitation transfer rate would largest when the energy difference between donor and acceptor triplet states is close to zero, as is observed experimentally [3]. In sharp contrast with that, it was first reported 50 years ago that for some donor-acceptor pairs with triplet energies well off-resonance, the experimental TET rate constant was much larger than expected [4]. This discrepancy, known as *non-vertical* TET, appears in the case of flexible acceptor molecules and was studied in great detail for the case of *cis/trans* stilbene as acceptor compounds [4]. Here we present a new interpretation of the *non-vertical* TET rate constant, based on recently developed [5] theoretical methods for the computation of accurate potential energy surfaces (PES) of all electronic species involved in the process. An expression for the TET rate constant is proposed, which is a function of the crossing rate between initial and final PES of the intervening states, and provides a quantitative relationship between triplet-state energy and structure factors controlling the reaction. In this way, the dependence of triplet quenching and *non-vertical* TET processes on molecular structure can be ascertained in great detail. In addition, the concept of reaction coordinate in triplet-triplet energy transfer reactions would be discussed.

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III JORNADAS IBÉRICAS DE FOTOQUÍMICA –
ABSTRACTS

POSTERS

POSTERS

PS-1 – Atmospheric Photochemistry of Anthropogenic $\text{CF}_3(\text{CH}_2)_2\text{CHO}$

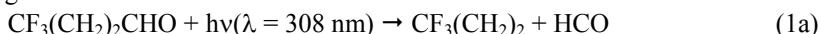
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$\text{CF}_3(\text{CH}_2)_2\text{CHO}$ is the major atmospheric degradation products of the CFC substitute, $\text{CF}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$, which is initiated by hydroxyl (OH) radical and chlorine (Cl) atoms. Additionally, $\text{CF}_3\text{C}(\text{O})\text{F}$ can be formed, which is hydrolyzed producing $\text{CF}_3\text{C}(\text{O})\text{OH}$, TFA [1,2]. High concentrations of TFA have been observed in contemporary water and air samples, suggesting the existence of one or more large unknown sources. To evaluate if UV photolysis of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ can be a source of TFA in the atmosphere, a complete photochemical study is required.

UV absorption cross sections (σ_λ) in the actinic region ($\lambda > 290$ nm) and the photolysis quantum yields ($\Phi_{\lambda=308 \text{ nm}}$) were determined in this work as a function of temperature (269–323 K) and pressure (75–760 Torr), respectively. Furthermore, the photodegradation products of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ were identified and quantified by FTIR spectroscopy in the presence of O_2 . All detected products in the pulsed laser photolysis of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ are consistent with the following channels:



Photolysis of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ mainly undergoes by C-C bond scission and, in a lesser extent, with channel (1c). Channel (1b) is negligible. Fluorinated acids were only detected in the absence of OH-scavenger (C_6H_{12}), indicating that OH radicals, and consequently, $\text{CF}_3(\text{CH}_2)_2\text{CO}$ radicals are formed in the system:



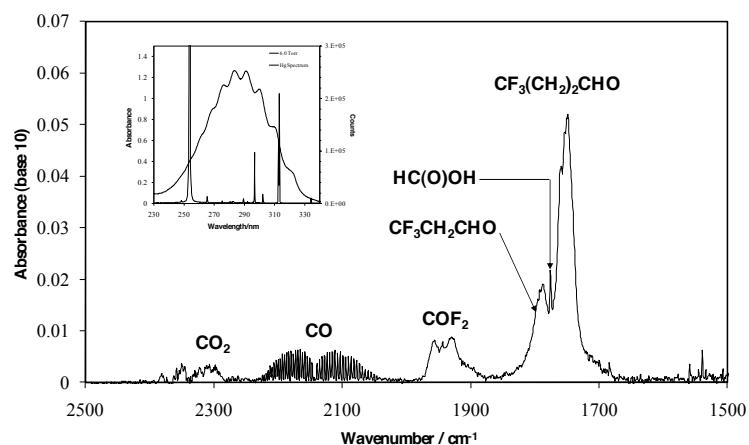


Figure 1. FTIR spectrum recorded after photolysis of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ at 308 nm in the absence of OH-scavenger. The gas-phase UV absorption spectrum of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ is depicted in the inset.

- [1] X. Tang, S. Madronich, T. Wallington, D. Calamari, *J. Photochem. Photobiol. B*, **46**, 83–95 (1998)
- [2] C. Georges, J. Y. Saison, J.L. Ponche, P. Mirabel, *J. Phys. Chem.* **98**, 10857-10862 (1994)

PS-2 – Photochemically driven addition of iminyl radicals to alkynyl Fischer carbene complexes

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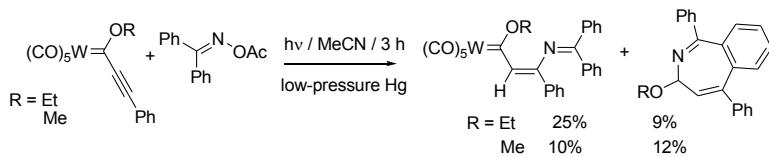
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Our research group have recently described [1] the use of acyloximes in the photochemical synthesis of heterocyclic compounds. First, the iminyl radical is easily generated by a nitrogen-oxygen bond cleavage. Then, the addition of this radical to unsaturated moieties gives heterocyclic compounds with ease in good yields.

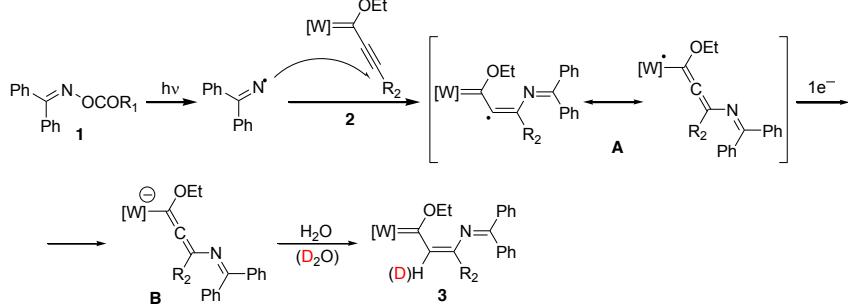
This fact, together with our experience in the photochemistry of imine Fischer carbene complexes [2], prompted us to study the reactivity of iminyl radicals with alkynyl Fischer carbene complexes.

Nowdays, we have shown the nitrogen-centered radical generated photochemically, is able to participate in a 1,4-addition to alkynylcarbene complexes to give a 5-aza-1-metalla-1,3,5-hexatriene, while radical 1,2-addition leads to azepines. (Scheme 1)



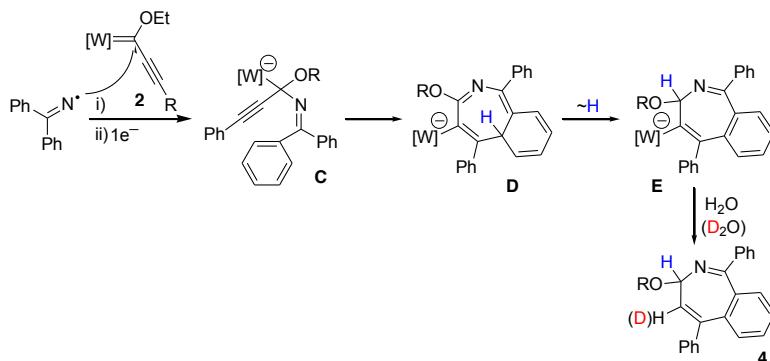
Scheme 1

We propose that irradiation of acyloxime **1** should generate the iminyl radical. This would attack carbene **2** at the alkynyl carbon (1,4-addition) to form intermediate **A**, which can be represented by two resonance structures (Scheme 2). A photoinduced electron transfer could then occur to give carbene anion **B**, which is able to react with traces of H_2O or D_2O to yield **3**.



Scheme 2

The formation of azepine **4** is thought to occur by subsequent 1,2-addition of the iminyl radical to the carbene carbon of **2** and photoinduced electron transfer to form the species **C** (Scheme 3). A 1,2-metal migration, promoted by the methoxy group, would cause simultaneous ring closure with one of the iminic phenyl groups to form intermediate **D**. A subsequent hydrogen shift regenerates the aromaticity and **4** would form after hydrolysis or deuterolysis.



Scheme 3

In summary, nitrogen-centered radicals, generated by the action of UV light, are capable of reacting with alkynyl Fischer carbene complexes in two ways, 1,2- and 1,4-addition giving interesting results.

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Acknowledgement: CSIC (Beca JAE/Predoc Alegria Caballero Millán), Universidad de La Rioja (API11/20)

PS-3 – Intramolecular photocyclization of vinyl iodides

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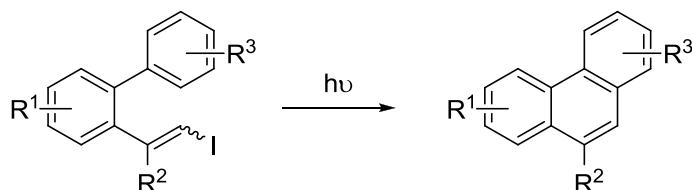
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In the context of our studies on photochemical reactions, we carried out the irradiation of *O*-aciloximes. This procedure allows us the preparation of several aza-heterocycles by intramolecular and intermolecular reactions [1].

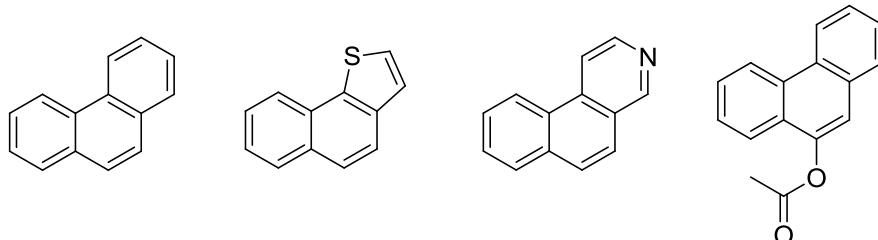
In the course of our research, we found of interest to carry out a similar investigation using vinyl iodides, with the aim of synthesize several polycycle structures.

The irradiation of vinyl iodides induces a homolytic C-I bond cleavage and the generation of a vinyl radical, which evolves adding to an unsaturated system to yield different polycycles.

Intramolecular reaction:



This photoreaction allowed us to obtain aromatic and heteroaromatic polycycle compounds easily, with several ring size and substituents [2,3].



[1] a) R. Alonso, P. J. Campos, B. García, M. A. Rodríguez, *Org. Lett.* **8**, 3521 (2006) b) R. Alonso, P. J. Campos, M. A. Rodríguez, D. Sampedro, *J. Org. Chem.* **73**, 2234, (2008) c) R. Alonso, A. Caballero, P. J. Campos, D. Sampedro, M. A. Rodríguez, *Tetrahedron* **66**, 4469 (2010)

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Acknowledgement: CAR (beca F.P.I de H. F. González-Cruz), Universidad de La Rioja (API11/20).

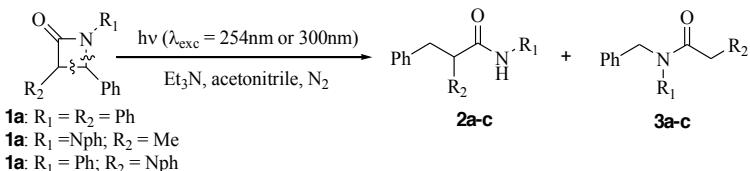
PS-4 – Light-Induced Ring Splitting of Azetidinones*Raúl Pérez-Ruiz, M. Consuelo Jiménez, Miguel A. Miranda**Departamento de Química-Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022, Valencia, Spain**e-mail:* rauprera@qim.upv.es

The chemistry of 2-azetidinones, also named β -lactams, has attracted considerable interest. This is mainly because this family of compounds is associated with a variety of biological activities; noteworthy their clinical application as antibacterial agents [1]. Therefore, many new synthetic methods for obtaining 2-azetidinone derivatives have been reported in the literature [2].

On the other hand, 2-azetidinones can be used as building blocks in organic synthesis exploiting the possibilities of ring cleavage at any of the four single bonds of the lactam ring. For instance, reductive 2-azetidinone cleavage has been achieved by palladium-catalyzed hydrogenolysis, whereas oxidative ring opening has been performed by treatment with ozone followed by reduction with NaBH₄ [3].

By contrast, the photoreactivity of 2-azetidinones has received much less attention as these compounds are generally photostable. Indeed, very few examples regarding light-induced ring splitting of 2-azetidinones have been found in the literature [4].

With this background, we are now interested in investigating the photoreduction of 2-azetidinones to gain further insight into mechanistic aspects. In particular, the aim of the present work is to study the photoreactivity of 2-azetidinones **1a-c** in the presence of triethylamine as electron-donor. Product studies confirmed that ring splitting of **1a-c** actually takes place, leading to open-chain amides (see Scheme below). Fluorescence, as well as laser flash photolysis experiments, have been carried out in order to elucidate the reaction mechanism.



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[2] See for example: (a) Singh, G. S.; D'hooghe, M.; De Kimpe, N. In *Azetidines, Azetines and Azetes in Comprehensive Heterocyclic Chemistry-III*; Katritzky, A. R., Ramsden, C. A., Scriven, E., Taylor, R., Eds.; Elsevier: UK, 2008; Vol. 2, p 1; (Stevens, C., Ed.); (b) Hwu, J. R.; Ethiraj, K. S.; Hakimelahi, G. H. *Mini-Rev. Med. Chem.*, **3**, 305 (2003); (c) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Rev.*, **107**, 4437 (2007).

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PS-5 – The photochemistry of 5-tert-butyl uracil

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Formation of pyrimidine dimers in DNA after UV irradiation has been demonstrated to be associated with deleterious biological effects. Therefore, a number of studies have been performed in order to understand the photochemistry of pyrimidines (Pyr). So far, three different types of Pyr dimers have been described as a result of UV-irradiation: cyclobutane pyrimidine dimers (CPDs), pyrimidine (6-4) pyrimidone photoadducts and thyminyl-dihydrothymines (spore photoproducts, SP) [1].

Formation of CPDs takes place through a formal [2+2] cycloaddition between the C5-C6 double bonds of two Pyr units. On the other hand, the (6-4) photoadducts are the result of a photoaddition between the carbonyl moiety of a Pyr and the C5-C6 double bond of another one, leading primarily formation of oxetane intermediates. As regards SP, they are the result of a formal linking between the allylic carbon of one Pyr to the C5 position of a neighbouring one. Although extensive mechanistic knowledge on Pyr dimer formation has been gained indeed, issues such as the lack of pyrimidine (6-4) pyrimidone formation or the special conditions required to obtain spore photoproducts from the triplet manifold should be explained [1, 2].

For this purpose, the photochemistry and photophysics of 5-tert-butyl uracil has been investigated. The presence of a bulky substituent at C5 is expected to prevent SP formation, according to theoretical calculations, it should disfavor the [2+2] cycloaddition leading to CPDs.

As a matter of fact, direct irradiation of the modified base, leads to a pyrimidine photoproduct, whereas triplet photosensitisation results in CPDs formation.

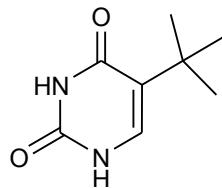


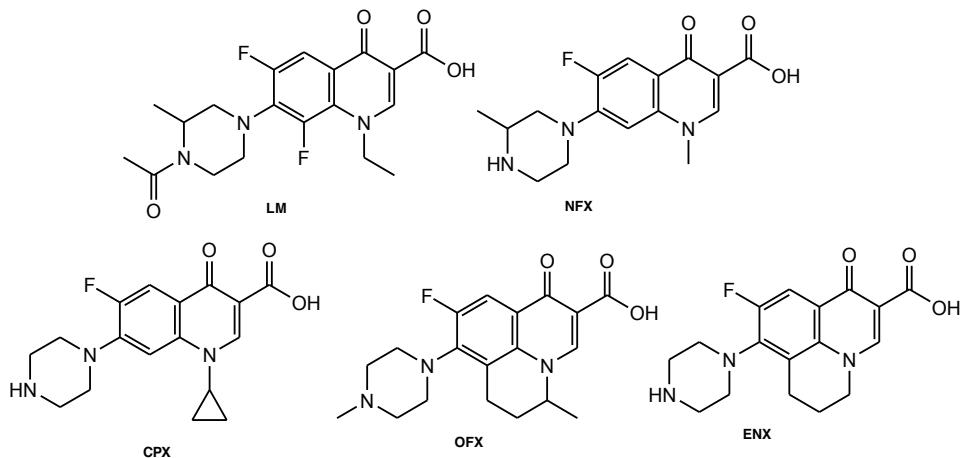
Figure 1. Structure of 5-tert-butyl uracil.

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PS-6 – Photoreactivity of fluoroquinolones with DNA*S. Soldevila, Francisco Boscá, M.A. Miranda**Instituto de Tecnología Química (UPV-CSIC), Avda. Los Naranjos s/n, 46022, Valencia,
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Fluoroquinolones (FQs) are well-established antibacterial drugs, whose pharmacological activity is associated with inhibition of the bacterial topoisomerase (DNA gyrase and topoisomerase IV). They have a fluorine atom attached at position C-6 of the bicyclic main ring; in some cases a second halogen is present at position C-8. Number of reports have shown that photosensitizers properties of FQs revealing that DNA is one of the most important biological targets for this effect [1]. Indeed, FQs are a family of drugs that besides to present phototoxic properties, has shown *in vivo* photocarcinogenicity [2].

To explain all these effects, have been done with several fluoroquinolones such as lomefloxacin (LM) enoxacin (ENX), ofloxacin (OFX), norfloxacin (NFX), and ciprofloxacin (CPX) a large number of photophysical and photochemical studies (Figure1).

**Figure 1.** Structure of fluoroquinolones

However there are few reports about the reactivity of FQs intermediates with DNA as well as dGuO (2-deoxyguanosine monohydrate), the most reactive nucleoside.

In this context a Laser Flash Photolysis (LFP) study in conjunction with fluorescence measurements, have been performed with monohalogenated quinolones such as ENX, NFX, CPX, OFX and the dihalogenated quinolone LM in the presence and absence of DNA as well as dGuO.

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Table 1. Photophysical properties of FQs in DNA or dGuo aqueous media

FLQ	$k_{T, \text{DNA}}^{\text{a}}$ (M ⁻¹ s ⁻¹)	$k_{T, \text{dGuO}}^{\text{b}}$ (M ⁻¹ s ⁻¹)	k_a^{c} (M ⁻¹)
CPX	6×10^7	1×10^8	543
ENX	4×10^7	1×10^8	400 ^d
NFX	2×10^8	6×10^7	476
OFX	1×10^8	1×10^8	152
NLX	1×10^8	2×10^7	-
LM	2500×10^9	8×10^8	258

^a k_T DNA; FQ triplet quenching rate constant by DNA, ^b k_T dGuO; FQ triplet quenching rate constant by dGuO, ^c k_a ; FQ-DNA association constants determined by fluorescence, ^dRef [4]

The rate quenching constants of FQs intermediates with DNA and dGuO were calculated to show important differences between LM and the monohalogenated fluoroquinolones (Table 1).

The FQs-DNA association constants result to be very simillars (Table 1).

FQs photobinding to DNA was also studied using a precipitation DNA test. The results were in accordance with those obtain by LFP.

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- [2] A. Albini and S. Monti *Chem. Soc. Rev.*, **32**, 238-250 (2003)
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- [4] S. Sortino and G. Condorelli, *New J. Chem* **26**, 250-258 (2002)

POSTERS

PS-7 – Study of potential fluorescence markers for β -amyloid aggregates

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Proteins are essential for life. They have the ability to fold into their native structure and maintain this condition to develop the corresponding functions. Under certain conditions, however, this folding may be incorrect, resulting in partial or total loss of functionality of this protein. This leads to diseases, such as the neurodegenerative Alzheimer disease, which is attributed to the accumulation of β -amyloid peptides in the form of fibers, although the early soluble oligomers are thought to be the primary toxic species rather than the insoluble fibrils [1].

Currently, Thioflavin T is the most used fluorescent marker for β -amyloid fibers, due to the huge increase of its fluorescence intensity in the presence of these structures. Nevertheless, it is not sensitive to smaller aggregates. In this work we study different dyes as potential fluorescence markers of amyloid fibers and especially of the early oligomers. Dyes of three families (imidazole, oxazole and thiazole) with structural similarities to Thioflavin T were chosen, all of them showing excited-state proton transfer.

Recently reported protocols were used first for the preparation of homogenous unaggregated β -amyloid samples and then for the controlled aggregation of the peptide to yield either oligomers or fibrillar aggregates [2]. The early amyloid aggregates were characterized as a function of incubation time and amyloid concentration using a fluorescent-labelled amyloid peptide with the technique of Fluorescence Correlation Spectroscopy (FCS). Then changes in fluorescence and anisotropy properties of the dyes under study due to the presence of early amyloid aggregates or fibrils were studied and compared to those of Thioflavin T. One of the imidazole derivatives is very sensitive to the formation of fibers whereas the oxazole and thiazole derivatives show great changes in their fluorescence intensity in the presence of the early small aggregates.

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PS-8 – Dansyl derivatives of cholic acid as tools to build speciation diagrams for sodium cholate aggregation

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Cholic acid (ChA) is the most abundant bile acid (BA) in humans. This family of water-soluble steroids exhibits an unusual cis fusion between rings A and B, a different number of hydroxyl groups in the α face, and a lateral chain ending in a carboxyl moiety. This structure results in facial amphiphilia; thus, their β convex face is hydrophobic, whereas the α concave face shows a more hydrophilic character; therefore, in aqueous solution, they tend to form aggregates that increase in size with concentration [1,2].

In this communication we have selected the fluorescent ChA derivatives to investigate its aggregation behavior. Concretely, dansyl (Dns) chromophore has been covalently attached at positions 3 α -, 3 β -, and 7 α - of ChA (Chart 1) [3].

By means of steady-state and time-resolved fluorescence the percentage of the different aggregates as a function of non-fluorescent sodium cholate (NaCh) has been established.

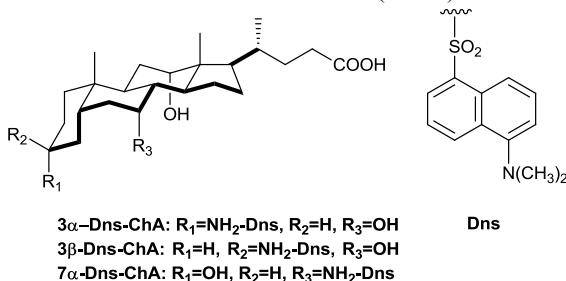


Chart 1. Structures of the Dns derivatives used for the characterization of ChA aggregates.

The UV-vis spectra of Dns-ChAs in aqueous NaCl (0.2 M) exhibited a maximum at around 330 nm and a shoulder at \sim 250 nm. The fluorescence spectra of the derivatives showed a maximum at \sim 550 nm and the fluorescence quantum yields are close to 0.05. Lifetimes of the singlet excited states (τ_s) ranged from 4.8 ns for 3 α - and 3 β -Dns-ChA to 7.4 ns for 7 α -Dns-ChA.

The behavior of the fluorescent ChA derivatives was examined in the presence of nonfluorescent NaCh. The fluorescence quantum yield increased with increasing concentration of NaCh for the three Dns-ChAs. Analogous experiments using Dns-Gly evidenced the importance of the covalent link between the dansyl chromophore and the steroid skeleton (Figure 1A).

Furthermore the fluorescence lifetimes of the Dns-ChAs derivatives increased in the presence of increasing concentrations of NaCh as a proof of their dynamic behavior (Figure 1B).

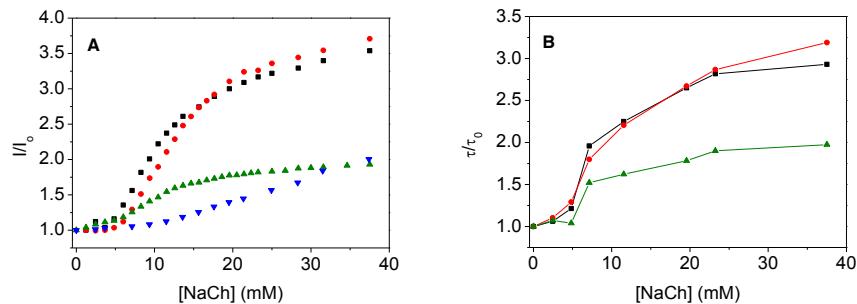


Figure 1. Changes in the relative emission (I/I_0) (A) and singlet lifetimes (τ/τ_0) (B) of 3α - (■), 3β - (●), 7α -Dns-ChA (▲) and Dns-Gly (▼) *versus* NaCh concentration in 0.2 M aqueous NaCl.

From the steady-state and time-resolved fluorescence experiments, three different regions can be observed that can be correlated with the presence of NaCh in solution, in the primary and secondary aggregates. These results are in excellent agreement with the aggregation model proposed by Small [4].

A further effort was made to exploit the combined steady-state and time-resolved photophysical experiments for Dns-ChAs to build the speciation diagram. Thus, the percentage of each component (%) at different concentrations of NaCh in 0.2 M aqueous NaCl was determined (Figure 2) [5].

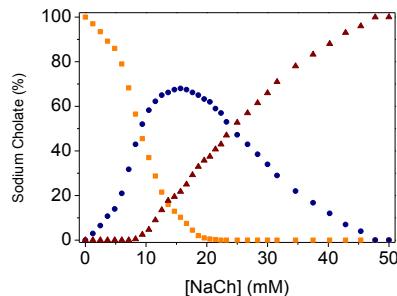


Figure 2. Percentage of NaCh in solution (■), in primary (●) and secondary aggregates (▲).

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- [5] M. Gomez-Mendoza, M. L. Marin, M. A. Miranda, *J. Phys.Chem. Lett.*, **2**, 782-785 (2011).

PS-9 – Exploring DNA intercalation through single-molecule RET

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Resonance energy transfer (RET) in ensembles of randomly-located donors and acceptors results in a distribution of donor fluorescence lifetimes [1]. Normally, this lifetime distribution cannot be reliably recovered from bulk time-resolved fluorometry, as several dissimilar distributions may provide a good fit to the donor fluorescence decay. Thus, the most advisable way of determining the donor lifetime distribution is through single-molecule measurements, capable of revealing heterogeneity and ubiquitous population distributions. Herein we report the influence of RET on the fluorescence lifetime distribution of DNA-attached Alexa Fluor 488 (AF488), acting as energy donor, upon binding of DNA intercalator YOYO-3, acting as energy acceptor. YOYO-3, a cyanine dimer fluorophore, is assumed to bind double-stranded DNA (dsDNA) through intercalation [2]. When the donor AF488 is linked at the dsDNA end, intercalation of YOYO-3 into the nucleic acid causes a multitude of randomly-distributed donor-acceptor distances. We have probed the effect of different YOYO-3 saturations on the AF488 lifetime distribution using single-molecule time-resolved fluorescence experiments.

We employed a 45 basepair (bp) dsDNA labelled at the 5'-end with the donor dye AF488. Solutions with picomolar concentration of this labelled DNA in the presence of increasing amounts of YOYO-3 (from 0 to 10^{-6} M) were studied using single-molecule time-resolved fluorescence spectroscopy. An inverted confocal microscope-based single-molecule fluorescence system was employed, with the unique feature of using picosecond-pulsed excitation laser and detection on Time-Tagged Time-Resolved (TTTR) mode [3]. The TTTR mode allows obtaining single-molecule fluorescence bursts, reconstructing the fluorescence decay histogram, as well as investigating the burst integrated lifetime distribution.

Figure 1 shows the distributions of lifetimes recovered for individual fluorescence bursts from AF488 labelling dsDNA, in the presence of increasing YOYO-3 concentrations. As expected, the increasing concentration of the intercalator leads to saturation of the dsDNA binding sites, resulting in an efficient shortening of the average distance between the donor at the 5'-end and the acceptor bound to the double helix. The results in Figure 1 are, hence, in agreement with a resonance energy transfer mechanism, by which the donor fluorescence lifetime is quenched, and the distribution shifts to shorter times with increasing acceptor concentration. Likewise, the distribution narrows at high acceptor concentrations, meaning that the energy transfer is very efficient towards the acceptor molecules that lie close to the donor. Donor-acceptor distance distributions, as well as energy-transfer efficiency distributions, were calculated from the fluorescence lifetime distributions. Alternatively, these distance and efficiency distributions were calculated from the proximity ratio [4], in order to draw a comparison between the results obtained through both methods.

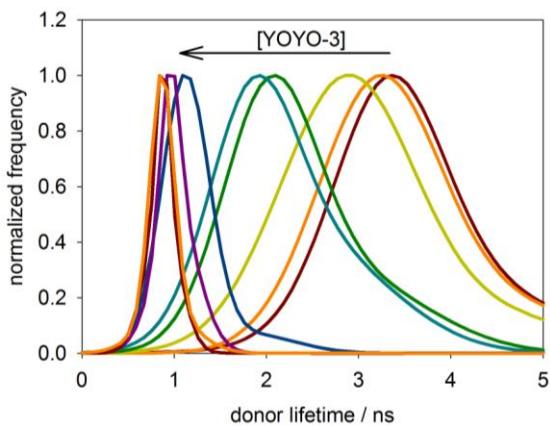


Figure 1. AF488 fluorescence burst lifetime distributions in the presence of increasing concentrations of YOYO-3, from 0.0 to 1.0 μM .

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Acknowledgement. Grants P07-FQM-3091 from the Consejería de Innovacion, Ciencia y Empresa (Junta de Andalucía), and PERG03-GA-2008-230917 from the 7th EU Framework Programme.

PS-10 – Semi-Empirical Model for Micellar Concentration in Surfactant Solutions. Solution Properties and Dye Exchange.

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Surfactant solutions are highly dynamic systems, where micelles (hosts) are in equilibrium with free surfactant molecules and both surfactant and dye molecules (guests) are being constantly exchanged between the aqueous solution and the micellar pseudo-phase.

Micellar systems can be studied with a big variety of techniques, such as conductivity of ionic surfactants, surface tension, NMR, light scattering, fluorescence spectroscopy and recently Fluorescence Correlation Spectroscopy (FCS) [1,2]. In spite of important advances in the theoretic description of the micellization process, no practical model for the concentrations of monomeric and micellized surfactants in a solution of a given total surfactant concentration has been proposed so far. Such a model is essential for a quantitative analysis of experimental data from micellar systems.

We present a new semi-empirical model directly for the monomeric and micellized surfactant concentration as function of the total surfactant concentration based on the phase separation model and probabilistic arguments [3]. We then use this model for a systematic description of a variety of physical properties which depend on the surfactant concentration. The model functions can be easily implemented in typical data analysis software and can be directly fitted to experimental data in order to obtain physical parameters, and especially the *cmc* itself.

We present the application to direct solution properties such as conductivity, NMR and surface tension. We also analyze the dye exchange equilibrium of a big variety of dyes with very different affinity to the micelles based on fluorescence titrations and diffusion coefficients measured by FCS.

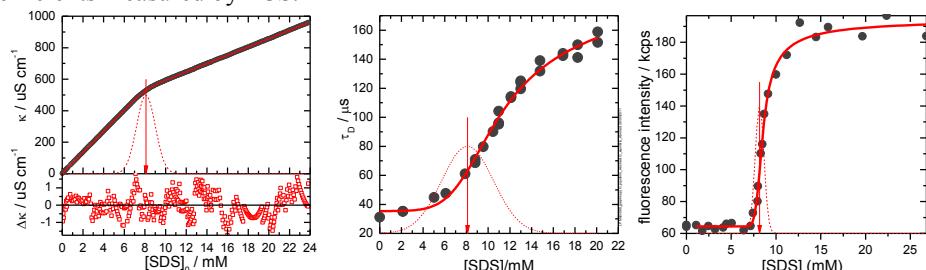


Figure 1. Conductivity, diffusion time, and fluorescence intensity of Cumarine 152 with SDS.

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PS-11 – Confined Photodynamics within the Human Serum Albumina Protein

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Nanocaging of organic as well as drugs may lead to large and significant changes in the spectroscopy and photodynamic of the molecular system [1-3]. The changes are generally reflected in blue shift of the emission spectra and longer fluorescence lifetime and related relaxation process.

Recently, we reported on the photodynamics of trisodium 8-hydroxypyrene-1,3,6-trisulfonate (pyranine, HPTS) interacting with the human serum albumin (HSA) protein and γ -CD in water solutions [4]. The results were interpreted in terms of ultrafast direct intermolecular-proton transfer (ESPT) between HPTS and amino acid residues, as well as slow dynamics of the water molecules around the protein residues. Here we report on the behavior of the parent molecule of HPTS, pyren-1-ol (pyrenol, HP) interacting with similar nanohosts.

The results presented here show changes in the photophysical and dynamical properties of the free HP upon addition of HSA, due to the hydrophobic interactions and confinement effect (Figura 1). The stoichiometry of the formed complex with the protein is 1:1 and the equilibrium constant is $1.84 \times 10^6 \text{ M}^{-1}$ at 293 K. From the ps-resolved experiments we found that the fluorescence lifetimes of the 1:1 entity become longer with respect to those measured for the free molecule (Figure 1C). The rotational times obtained from the anisotropy measurements indicate strong confinement in the robust HP:HSA complex. In addition to that we observed that this kind of complexes undergoes an energy transfer process from the excited tryptophan 214 (Trp214) of HSA to the trapped HP, which occurs with an efficiency of 77%, and calculated distance between the donor and the acceptor of 18 Å.

In contrast to HPTS behavior, HP shows a weak ground state population of the anion in water solution (pH 7). Upon encapsulation by the HSA protein, ground state complexes are observed for both molecules, indicating direct interaction these dyes with the protein residues. The ESPT reaction of the encapsulated HP is slower (400 ps) with comparison to HPTS (130 ps). This is explained in terms of the lower pK_a^* of HP ($pK_{a(HPTS)}^*=0.6$, $pK_{a(HP)}^*=4.5$).

We believe that these results will contribute for a better understanding of the processes occurring in encapsulated drugs and this should be relevant to nanopharmacodynamics.

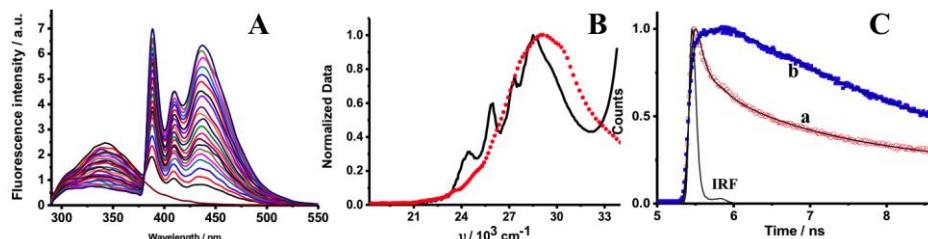


Figure 1. A) Emission spectra of $7 \mu\text{M}$ HSA in buffer (pH=7) and in the presence of different amounts of HP $\{(0-2) \times 10^{-5} \text{ M}\}$. The excitation wavelength was 280 nm. B) Spectral overlap between HP absorption (—) and HSA emission (...) in a phosphate buffer solution (pH 7). The two spectra are normalized at their respective maxima. C) Emission decays of (a) HP in buffer (pH7) and in the presence of (b) $1.6 \mu\text{M}$ HSA observed at 450 nm and excited at 371 nm.

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Acknowledgment: This work was supported by MICINN through projects MAT2008-01609, and Cyclon Network (MRTN-CT-2008-Project 237962). B.C. thanks the MICINN for the Ramon y Cajal contract.

PS-12 – Photophysical Behavior of Systems Containing Benzophenone and Naphthalene Chromophores

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Benzophenone (BZP) and naphthalene (NPT) are classical textbook examples of photoactive chromophores, which can undergo a number of photophysical and photochemical processes. Transient species generated upon excitation of BZP and NPT are detectable by the usual emission or absorption spectroscopies, and their main features have been described in detail.

Specifically, BZP exhibits several remarkable characteristics that make it very useful for photochemical studies. Thus, the presence of an absorption band at $\lambda > 320$ nm allows selective BZP excitation in the presence of a large number of organic substrates (and therefore its use as photosensitizer); besides, the intersystem crossing quantum yield (ϕ_{ISC}) is close to the unity, which makes BZP a suitable “triplet source” for T-T energy transfer to substrates with lower E_T . On the other hand, both the lowest triplet excited state ($n\pi^*$, $E_T = 69$ kcal/mol, $\lambda = 525$ nm) and the benzhydryl radical ($\lambda = 550$ nm) are observable in the transient absorption spectrum obtained upon laser flash photolysis (LFP) in acetonitrile [1,2].

Concerning NPT, emission from the first singlet excited state (${}^1\text{NPT}^*$, $E_S = 92$ kcal/mol, $\phi_F = 0.19$) is centred at 340 nm, although longer-wavelength fluorescence from NPT excimers has also been reported. Intersystem crossing leads to ${}^3\text{NPT}^*$, which exhibits a maximum at *ca* 430 nm in the LFP spectrum. Under specific experimental conditions, the radical cation (NPT^+) can also be detected (≈ 600 nm) [3,4]. Delayed P-type fluorescence in NPT derivatives may arise from interaction of two molecules in the triplet state (${}^3\text{NPT}^* + {}^3\text{NPT}^*$, triplet-triplet annihilation) thus producing one NPT molecule in the excited singlet state. The lifetime of this biphotonic process, which is usually observed by emission measurements upon direct irradiation of NPT, is half the value of that found for the concomitant phosphorescence [5,6].

Photoprocesses occurring in systems containing both chromophores have attracted considerable attention in the past. Upon long-wavelength excitation of BZP in the presence of NPT, the expected intermolecular T-T energy transfer from ${}^3\text{BZP}^*$ to NPT does actually takes place. In addition, formation of ${}^3(\text{BZP}/\text{NPT})^*$ triplet exciplexes constitutes an efficient channel for ${}^3\text{NPT}^*$ deactivation. Bichromophoric compounds containing covalently linked BZP and NPT units have also been investigated; similar deactivation pathways have been proposed for these dyads, albeit with kinetics markedly faster than in the intermolecular case [7].

In the present work, we wish to report on the direct LFP observation of the characteristic ${}^1\text{NPT}^*$ emission in the microsecond time domain, upon selective excitation of the $n\pi^*$ carbonyl band in BZP/NPT systems (Figure 1).

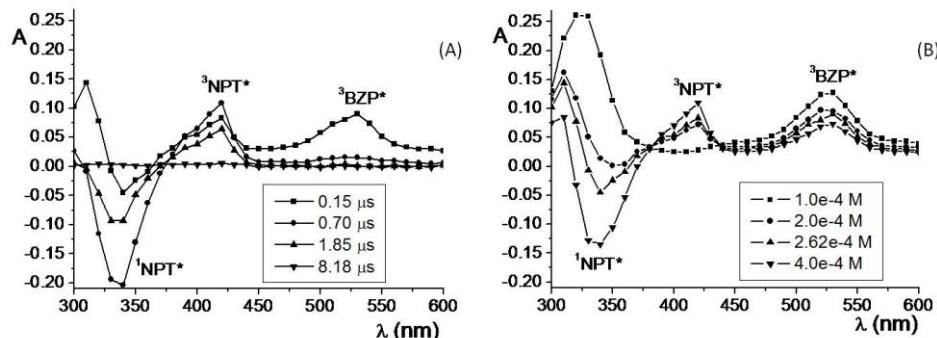


Figure 1. Laser flash photolysis of BZP (2.6×10^{-3} M) in acetonitrile/ N_2 at $\lambda_{exc} = 355$ nm. **(A)**: Spectra obtained in the presence of NPT (2.6×10^{-4} M) at different time windows (0.15, 0.70, 1.85 and 8.18 μ s). **(B)**: Spectra recorded in the presence of increasing amounts of NPT ($1.0-4.0 \times 10^{-4}$ M) 0.15 μ s after the laser pulse.

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PS-13 – Photoprotection in Acylated Anthocyanins

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Both natural anthocyanins and synthetic 7-hydroxyflavylium ions convert the absorbed radiation into heat by fast (5–25 ps) excited-state proton transfer (ESPT) from the flavylium cations to water followed by rapid decay of the resultant excited base, with overall quantum efficiencies greater than 0.99. Consequently, for free anthocyanins, ESPT can serve as an efficient photoprotection mechanism. Natural anthocyanins absorb mainly in the visible part of the spectra with only a narrow band in the UV-B (ca. 280 nm) so this highly efficient mechanism of deactivation protects the plant essentially from visible light. The red flavylium cations of anthocyanins form ground-state charge-transfer complexes with several naturally occurring electron-donor copigments that exhibit high UV-B absorptivities but have no comparable deactivation mechanisms. Acylation of anthocyanins with the same copigments results in the formation of intramolecular complexes with increased UV absorbance.

In this work, we study the intermolecular complex of cyanin (Cy) with p-coumaric acid (Coum) and of the naturally occurring acylated anthocyanin, cyanidin-3-O-[6''-O-(E-p-coumaric)-2''-O-(β-xylopyranosyl)-β-glucopyranoside]-5-O-β-glucopyranoside (CyCoum) in which there is the possibility of formation of the analogous intramolecular copigmentation complex (Fig. 1).

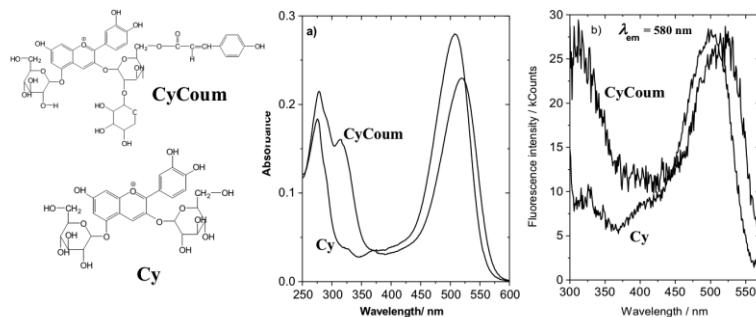


Figure 1. Molecular structures, (a) absorption and (b) fluorescence excitation spectra with emission at 580 nm of Cy and CyCoum in aqueous solutions, pH 1.

Absorption (Figs. 1a) and fluorescence excitation spectra measured at the emission wavelength of the flavylium (Figs. 1b) show efficient energy transfer from the Coum to the Cy moieties.

The fluorescence decays of CyCoum and Cy measured with ps-resolution are quasi-single exponential at the emission wavelengths of the acid and base forms, the pre-exponential

coefficient of the residual longer decay times (ca. 120 ps) being two (Cy) or three (CyCoum) orders of magnitude lower.

The ratio of the short decay times ($\tau_{\text{Cy}}/\tau_{\text{CyCoum}} = 5.0/4.1 = 1.2$) is significantly smaller than the ratio of fluorescence quantum yields ($\phi_{\text{Cy}}/\phi_{\text{CyCoum}} = 2.3$), which suggests the presence of an additional undetected shorter decay time in the fluorescence decay of CyCoum responsible for the discrepancy (“static” quenching).

The presence of short (sub-ps) times in the decays of Cy and CyCoum was investigated using fs-laser flash-photolysis (upconversion). The major difference with respect to the ps-data is the presence of short decay times (ca. 1 ps) with large pre-exponential coefficients (ca. 0.8) for both compounds, which was expected for CyCoum, but not for Cy.

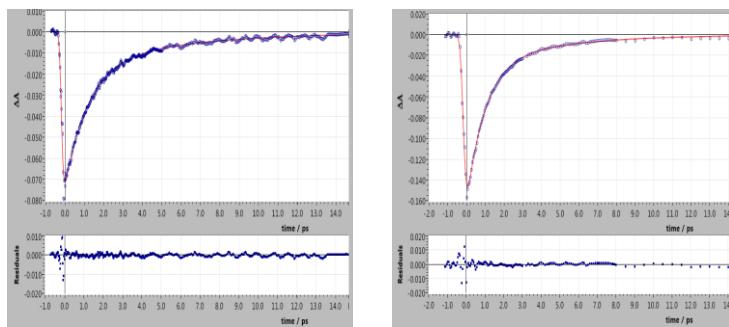


Figure 2. Recovery of the integrated absorption band, 505-535 nm for Cy and 510-540 nm for CyCoum, as a function of time.

The observation of an additional shorter recovery time for both compounds, not detectable with ps resolution, suggests that the deprotonation process (the only one existing for Cy) cannot be described by a single exponential. These data adds three important pieces of information. First, by replacing the short decay time observed with ps-resolution by the two detected recovery times, the fluorescence ratio calculated from the time resolved data, 2.3, becomes identical to the experimental steady-state fluorescence ratio $\phi_{\text{Cy}}/\phi_{\text{CyCoum}} = 2.2$. Second, because proton transfer should be identical in Cy and CyCoum, the shorter times observed with CyCoum likely reflect the contribution of internal conversion [1,2] to the deactivation to the ground state of the complexed AH^{+*} . This hypothesis is supported by the blue shift during recovery of CyCoum., which indicates that the complexed form returns to the ground state faster than the uncomplexed one. Finally, although this contribution does not seem very important to the efficiency of photoprotection, the additional energy absorption in the UV brought about by the coumaric moiety, which is transferred to the Cy moiety, followed by deprotonation of the flavylium cation, provides an elegant protection from excess UV-light.

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PS-14 – Photophysical characterization of F8BT10. Structural relaxation and energy transfer studied by ultrafast time-resolved fluorescence

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Conjugated organic polymers control the processes of charge recombination in many polymer based light emitting diodes, and one important question in the area of LEDs is what happens in the deactivation of their excited states. These polymers frequently show complex fluorescence decays in which fast decay/rise times containing information on processes resulting from excitation, such as solvent and/or conformational relaxation [1], and energy transfer, are commonly observed.

In the last years, we have studied the photophysical properties of several polyfluorenes (PFO) [2]. Following this line of investigation, now we report the photoluminescence properties of the polymer (9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1,3}-thiadiazole), F8BT10. This polymer constitutes a useful model system to understand how the F8-BT system couples with respect to orbital delocalization, energy and/or electron transfer, and to investigate how side-chains affect conformational relaxation of the polymer.

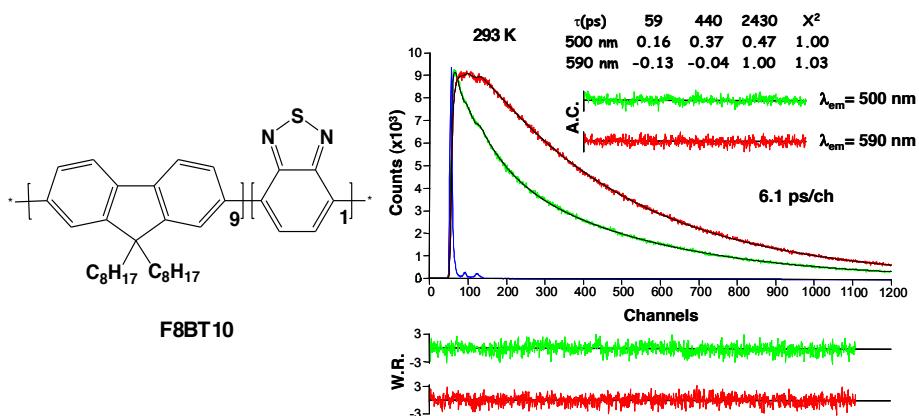


Figure 1. Chemical structure of F8BT10, and global analysis of fluorescence decays in MCH.

The picosecond time-resolved fluorescence measurements seem to indicate that there is not energy transfer between the two components of the polymer, from F8 to BT, nor detectable exciton quenching which could result from excited state charge transfer. However, the fluorescence quantum yield measured for F8 in the polymer is significantly reduced (by more than 60%) in comparison to that of the same polymer without BT, suggesting an important loss of energy from the fluorene chain segments. The energy transfer from F8 segments to BT units could occur via both exchange and dipole–dipole intrachain energy

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transfer, the last resulting from the large spectral overlap between F8 emission and BT absorption. In the fluorescence decays, the two major decay components (see Fig.1) represent the fluorescence lifetimes of F8 (440 ps) and BT (2.43 ns), while the shortest decay time (ca. 60 ps in methylcyclohexane) was attributed to conformational relaxation of the polymer backbone on the basis of its dependence on temperature and solvent viscosity. The structural relaxation leads to more planar polymer conformations, with smaller fluorene-fluorene dihedral angles in the excited state.

The photophysical behaviour of F8BT10 was also studied in PMMA solid film. The F8 emission spectrum decreased by almost 50-fold in intensity, strongly indicating the possibility of interchain energy transfer. The radiative energy transfer provides an alternative mechanism to populate the lowest energy polymer segments. The BT emission was strongly red-shifted (17 nm) relative to methylcyclohexane, which is also consistent with an increased planarization of the polymer in the film. Since conformational relaxation does not occur in solid films,³ the effects of radiative and non-radiative energy transfer in the film can be observed separately from other phenomena.

We believe that these studies may be helpful to elucidate the relative contributions of interchain and intrachain energy transfer processes in conjugated polymer thin films and then optimise energy migration in photonic devices.

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Acknowledgement. Roberto Di Paolo acknowledges the Fundação para a Ciência e Tecnologia, Portugal, for financial support (PTDC/QUI/65474/2006, co-financed by FEDER).

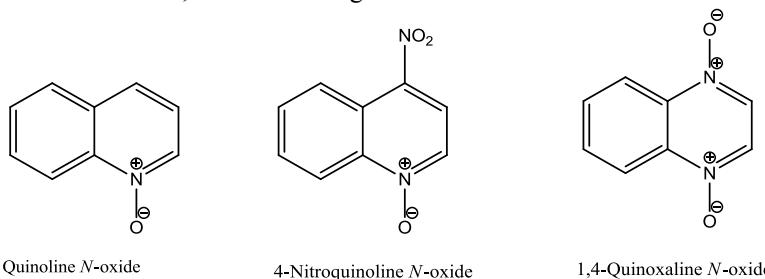
PS-15 – Photophysical characterization of heterocyclic N-oxides*N. Duran-Giner, S. Encinas, M. A. Miranda**Departamento de Química/Instituto de Tecnología Química, Camino de Vera s/n,
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Imino *N*-oxides exhibit a rich and complex photochemistry. Their photochemical reactions have been of interest since the beginning of the sixties, and their significance has not been limited to synthetic achievements. Among the biological applications, photoinduced oxidative DNA damage by heterocyclic *N*-oxides becomes relevant. The carcinogenicity and mutagenicity of substituted quinoline 1-oxides and diverse quinoxaline di-*N*-oxides, as well as their interaction with DNA have been demonstrated in numerous studies [1]. One of the interesting properties of those compounds is their ability to bind to DNA via charge-transfer in an aqueous solution [2].

On the other hand, it is also reported that the triplet excited state is involved in the photodeoxygenation of heteroaromatic *N*-oxides and not in their rearrangement [3].

In this context, despite the numerous studies on these oxygenated compounds, the general mechanism of oxygen transfer has not been fully elucidated as yet.

The aim of this research is a further characterization of the photophysical processes that are taking place from the *N*-oxides triplet state. For that purpose, several aromatic heterocyclic *N*-oxides have been studied, as shown in Figure 1.

**Figure 1.** Aromatic *N*-oxides studied

In this work, laser flash photolysis studies have been performed on different compounds to determinate the actuation mechanism of the *N*-oxide substrates depending on the structural features. Oxygen and solvent effect as well as electron, hydrogen and/or proton donors have been investigated to a further oxygen transfer mechanism knowledge.

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PS-16 – Excited-State Dynamics and Thermochromism of Poly(3-Hexylthiophene) (P3HT) in Solution

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The fluorescence decays of a stereo-regular HT poly-(3-hexylthiophene), P3HT, in methylcyclohexane (MCH) are described by sums of three or four exponential terms, respectively above and below -10 °C. In the high temperature region, the polymer lifetime (ca. 500 ps) [1] is accompanied by two shorter decay times (ca. 20 and 120 ps), which are assigned to intrachain energy transfer from high to lower energy excitons on the basis of temperature and wavelength dependence of the fluorescence decays (Figure 1). The absence of conformational (torsional) relaxation is attributed to the small dihedral angle between monomers that is predicted for the stereo-regular polymer in the ground state.

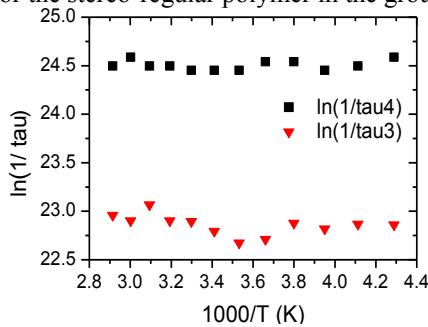


Figure 1. Arrhenius plots of (a) the reciprocals of the two shortest decay times $1/\tau_4$ and $1/\tau_3$.

Below -10 °C, the polymer forms excimer-like aggregates, showing vibrational structured absorption and emission bands similar to those observed in films. The vibrational structure is attributed to a deep minimum in the ground state energy surface of the dimer or aggregate. Below -40 °C, the fluorescence measured at the aggregate emission wavelength (670 nm) basically results from direct excitation of the aggregate, and decays with a sum of three exponential terms (decay times ca. 0.14, 0.6 and 1.5 ns, with similar weights).

Because the spectral similarities between film and aggregates indicate similar electronic first singlet excited states (and oscillator strengths), the much shorter decay times (0.4, 1.4 and 27 ps) and lower fluorescence quantum yield of P3HT in films are assigned to efficient exciton dissociation competing with radiative decay (ca. 1 ns).

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Acknowledgement. This work was supported by Fundação para a Ciência e Tecnologia (FCT), Portugal, project PTDC/QUI/65474/2006.

PS-17 – Evaluating the Energetics of the Proton Transfer for a 7-Hydroxyflavylium Salt in Water-Dioxane Mixtures

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The temperature dependence of excited state proton transfer reactions (ESPT) in water and in binary water-dioxane mixtures has been investigated employing the synthetic flavylium salt 7-hydroxy-4-methyl-flavylium chloride (HMF). In water at T = 20 °C, the ESPT mechanism involves solely the first excited acid AH^{**} and base A* forms of HMF and its acid form deprotonates to the solvent [1,2] in ca. 5 ps and pK_a* = -0.81. By adding 1,4-dioxane to the solvent-reactant water the decays become triple-exponential. The third exponential term is consistent with the presence of the geminate pair (Figure 1), and becomes detectable as a result of the increase of the recombination rate constant k_{rec} of (A*...H⁺) with the increase of the mole fraction of 1,4-dioxane.

All the rate constants for ESPT have shown a temperature-dependence in water and binary water-dioxane mixtures (mole fraction of 1,4-dioxane up to 0.5). However, the deprotonation rate constant k_d shows a non-Arrhenius dependence on temperature in both water and water-dioxane mixtures. The overall rate constant k_d is a sum of two distinct processes. At low temperatures (T from near freezing point until T ca. 15 °C) k_d is close to the dielectric relaxation rate of the solvent and has a barrier of ca. 3 kcal/mol, suggesting that the solvent reorganization is the rate-limiting step. At high temperatures (T > 25 °C) the proton transfer process resulting in the formation of the geminate pair is much less activated (nearly barrierless) and solvent-dependent [3].

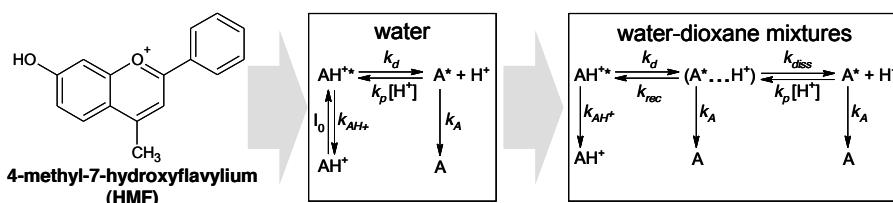


Figure 1. Flavylium salt studied and mechanisms involved in the excited state proton transfer in water and water-dioxane mixtures as a function of temperature.

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Acknowledgements. Fundação para a Ciência e Tecnologia (FCT) – Portugal, GRICES-CAPES 2006 program.

PS-18 – Characterization of the triplet excited state of bioactive compound thiabendazole

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Benzimidazoles (BZs) are a family of heterocyclic compounds that have shown a broad spectrum of anthelmintic activity and are effective as anti-nematode and anti-protozoal agents [1]. In addition, many of them are used extensively on fruits and vegetables as post-harvest fungicide [2]. In the last years many members of the family has attracted considerable attention due to its anti-tumoral behavior [3].

The biological action of benzimidazoles is, many times, limited by their low water solubility. Different strategies have been developed for improved the solubility of this biocides. Among they, formation of cyclodextrin drug complexes are frequently used by pharmaceutical industry to enhance the bioavailability of poorly soluble drugs

The thiabendazole (**1**) is a bioactive benzimidazole used as human and veterinary anthelmintic. The aim of the present work is the full characterization of photophysical properties of **1** triplet. This knowledge is an essential requirement to check the possibility of using thiabendazole as a probe for cyclodextrin complexation.

Thus, laser flash photolysis ($\lambda = 266$ nm) of deaerated acetonitrile or PBS/MeCN (3/1, v/v) solutions of **1** led to transients absorbing in the 350-700 nm range. The spectra obtained after the laser pulses shows a broad band centred at 570 nm assigned, in principle, to the T-T absorption (Figure 1). The lifetime was found to be 1 μ s in acetonitrile and 10.3 μ s in aqueous solution.

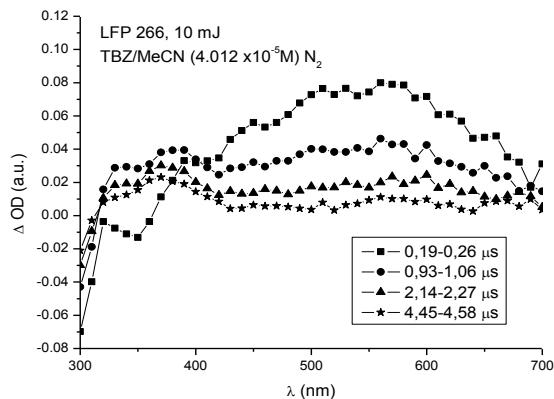


Figure 1. Transient absorption spectra obtained upon 266 nm excitation of **1** in acetonitrile

The value of the triplet energy of the thiabendazole is 289 KJ mol⁻¹, using Sandros equation.

The intersystem crossing quantum yield (Φ_{ISC}) of thiabendazole in PBS/MeCN was determinated from the ΔA of the T-T bands of isoabsorptive solutions of **1** and, the molar absorption coefficients of their triplets and the known ISC quantum yield and results is 0.91.

In order to study the influence of microheterogeneous media on the nature and behavior of the triplet excited state, **1** was included in α , β and γ cyclodextrins (CD) [5]. Normalized decays were monitored at 570 nm (Figure 2), and the triplet lifetimes are 12.2 μ s, 14.2 μ s, 9.5 μ s for α , β and γ CD, receptivity. These changes in photobehavior are attributed to the restrictions on the mobility of included **1** imposed by the cyclodextrin structure.

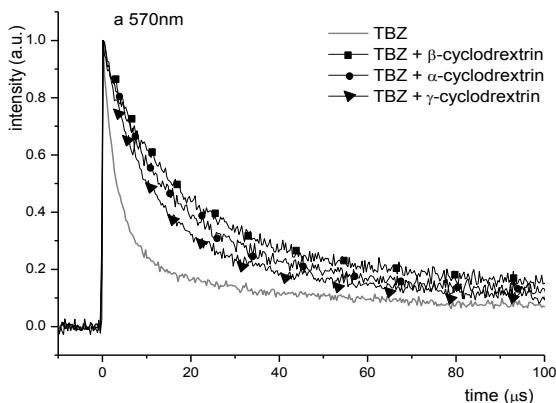


Figure 2. T-T absorption decay of **1** in different cyclodextrins at 570nm

The nature of the singlet and the triplet excited states and his ground state geometry of TBDZ was analyzed. The theoretical calculations are in both cases $\pi\pi^*$.

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Acknowledgement: Financial support from the Generalitat Valenciana (Prometeo Program) is gratefully acknowledged.

PS-19 – Photophysical and Photochemical Studies of Carprofen-Carprofen Dyads

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Dyads containing two covalently attached active chromophores have been used as model systems to gain mechanistic insight into some fundamental aspects of photochemical and photobiological processes, such as exciplex formation, energy, electron or proton transfer, etc [1].

The main photoreaction pathway of carprofen (CPF) is dehalogenation through a self-quenching mechanism. Electron transfer by self-quenching of ${}^3\text{CPF}^*$ leads to a radical ion pair. The radical cation deprotonates to the neutral carbazoyl radical, while the radical anion loses chloride (Figure 1) [2].

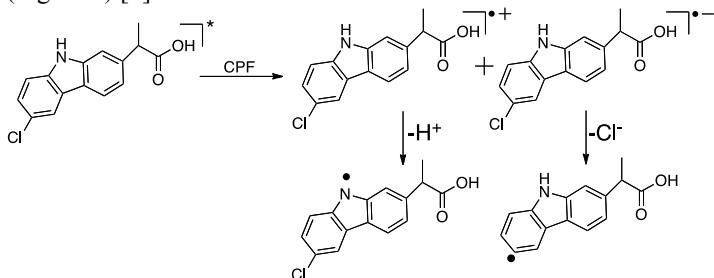


Figure 1. Electron transfer through self-quenching of ${}^3\text{CPF}^*$.

In order to get a deeper insight into the mechanism of this process, we have prepared diastereomeric dyads containing two CPF units (Figure 2). The length of the linker could be long enough to prevent the required spatial arrangement between the two CPF units for electron transfer, thereby facilitating the involvement of other competitive deactivation pathways.

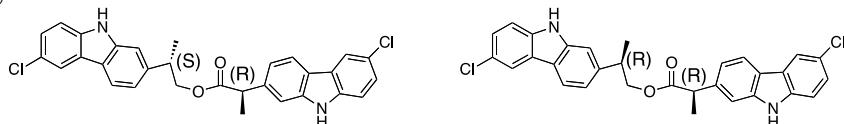


Figure 2. Structures of (SR)- and (RR)-CPF-CPF dyads.

[1] See for example: (a) M. C. Jiménez, M. A. Miranda and R. Tormos, *Chem. Soc. Rev.* **34**, 783 (2005), (b) I. Andreu, I. M. Morera, F. Bosca, L. Sanchez, P. Camps and M. A. Miranda, *Org. Biomol. Chem.* **6**, 860 (2008), (c) V. Lhiaubet-Vallet, M. C. Jiménez and M. A. Miranda, *J. Phys. Chem. B* **111**, 423 (2007), (d) I. Vayá, C. J. Bueno, M. C. Jiménez and M. A. Miranda, *Chem. Med. Chem.* **1**, 1015 (2006).

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**PS-20 – Photoprototropic Reactions of Hydroxycoumarins.
The “Push-pull” vs. the “Eigen pair” Mechanisms**

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The prototropic reactions of the first excited singlet state of 3-chloro-4-methylumbellifерone (3Cl4MU) [1], in water and dioxane:water mixtures (Dx:H₂O), are investigated using ps- and fs-time-resolved fluorescence techniques. The data revealed the presence of a fourth kinetic species, kinetically coupled to the neutral (N^{*}), tautomeric (T^{*}) and anionic (A^{-*}) forms of 3Cl4MU (Figure 1): the geminate (A^{-*}···H⁺) ion pair (Eigen pair).

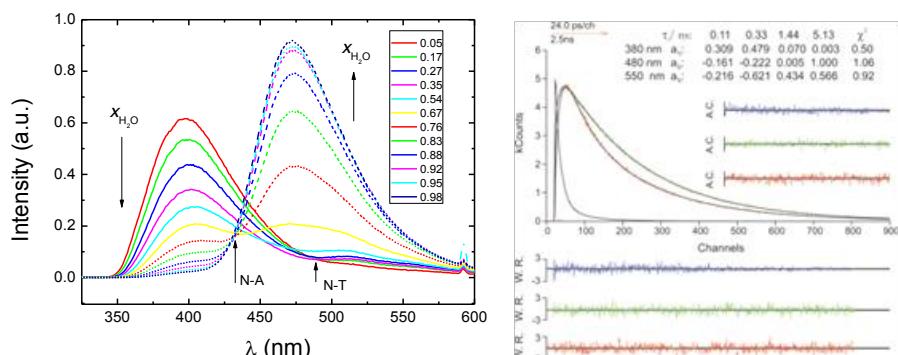
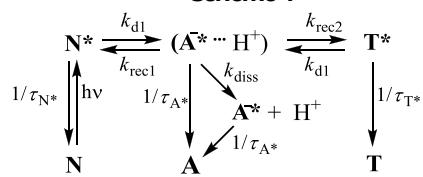


Figure 1. Steady-state (a) and time-resolved (b) fluorescence of 3Cl4MU in a Dx:H₂O mixture ($x_{\text{H}_2\text{O}}=0.76$), collected at 380, 480 and 550 nm (N^{*}, A^{-*} and T^{*} emissions dominant).

In Dx:H₂O mixtures, the free A^{-*} is not detectable when the mole fraction of water ($x_{\text{H}_2\text{O}}$) is less than 0.5 because the dissociation of (A^{-*}···H⁺) cannot compete with its recombination to give N^{*} or T^{*}. Above $x_{\text{H}_2\text{O}} = 0.7$, A^{-*} starts to become the dominant species at the expenses of (A^{-*}···H⁺). The solution of the 4-species kinetic system obtained in this work provided values for the eight rate constants involved (Scheme 1).

Scheme 1



The overall data have shown that the so-called “push-pull mechanism”, which assumes direct proton transfer between the two prototropic sites of hydroxycoumarins through a bridge of hydrogen-bonded molecules of water, is not likely to be the mechanism present with this system. Instead, the formation of T^* from N^* , apparently bypassing A^* , occurs via recombination of $(A^* \cdots H^+)$ to give T^* .

[1] J. Seixas de Melo, C. Cabral; J. C. Lima; A. L. Maçanita, *J. Phys. Chem. A*, 2011 (accepted)

PS-21 – Inter- vs intramolecular excimer formation in π -conjugated scaffolds substituted with 1-(pyrenylethynyl) units.

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In the last 30 years, π -conjugated polymers have been regarded as promising materials for the development of several electronic devices such as light emitting diodes (LED's), photovoltaic and solar cells, chromic devices, chemical sensors and non-linear optical systems.¹ Among these materials, poly-phenylacetylenes have been widely studied because they exhibit interesting chemical and physical properties due to their extended π -conjugated backbone. Their opto-electronic properties vary remarkably depending on the degree of conjugation length and the arene substitution patterns between the consecutive units. On the other hand, pyrene is an efficient fluorescent probe which has been successfully used as a molecular label in the study of a huge variety of molecules. Previous works of di(1-ethynylpyrene)s have shown that the rigidity of the connector bridge between pyrene units affects the formation of *intra-* and *intermolecular* excimers.² In this work, we study the optical properties of several bis(1-ethynylpyrene) compounds with different poly-phenylacetylene backbones as function of its length and the substitution patterns. A synthetic route combining Sonogashira couplings has provided a superior access to the target molecules.

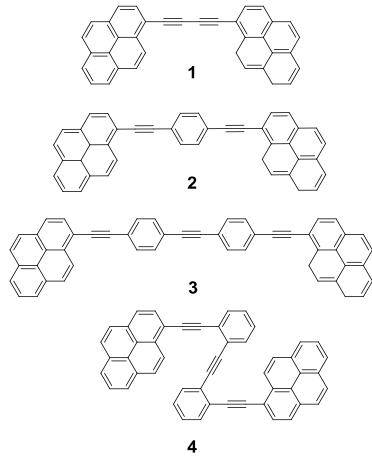


Figure 1. Di(1-ethynylpyrene) compounds studied with different conjugated-path length and substitution pattern.

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[2] A. C. Benniston *et al. Eur. J. Org. Chem.* 2272-2276 (2004)

PS-22 – Ultrafast photochemistry of biological chromophores and their water clusters.

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Indole, pyrrole, imidazole and phenol are the chromophores of important nucleobases and aromatic amino acids, such as histidine, tryptophan, allowing nucleic acids and proteins to absorb in the near UV part of the spectrum. In addition to the $\pi\pi^*$ transitions responsible for the strong UV absorption, in these aromatic rings containing heteroatoms, $\pi\sigma^*$ states excited states with dissociative character along the X-H coordinate (X=N, O) are also found at low energies. Although these states present very low oscillator strength, they are thought to play a key role in the photophysics and photochemistry of life building blocks.

Theoretical studies predict that the dynamics of these molecules after excitation along the $\pi\pi^*$ transitions is governed by $\pi\pi^* \rightarrow \pi\sigma^*$ non-radiative coupling via a conical intersection that populates $\pi\sigma^*$ state [1]. There the X-H bond starts to elongate until a second intersection with the ground state is met, leading to ultrafast internal conversion to the ground state and direct dissociation on the $\pi\sigma^*$ surface. These hypotheses have been partially confirmed by experiments able to detect the formed H-fragments [2-4]. Although the H atom detection experiments provide a valuable piece of information, measurements of the dynamics on the parent molecule are essential to attain a general view of the effective role of the $\pi\sigma^*$ state.

Herein we present the first femtosecond resolved experiments with parent ion detection, with the required sensitivity to measure simultaneously major and minor relaxation channels. The technique has been successfully applied to the mentioned chromophores and their water clusters, allowing us to provide a general view of the dynamics involving $\pi\sigma^*$ surfaces. Other phenomena, as the adiabatic excitation by the ultrashort pulses of higher electronic excited states and the coupling between $\pi\pi^*$ states are also observed and discussed.

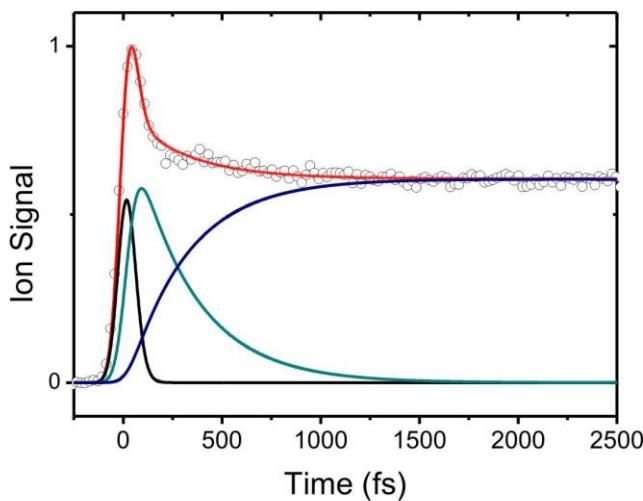


Figure 1. Indole⁺ transient signal after excitation at 248 nm. Solid lines correspond to a kinetic model based fit and its components: $\tau_1=22$ fs (coupling between $\pi\pi^*$ states), $\tau_2=320$ fs (dynamics involving the $\pi\sigma^*$ surface), $\tau_3>100$ ps (internal conversion).

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- [2] M. N. R. Ashfold, B. Cronin, A. L. Devine, R. N. Dixon, M. G. D. Nix. *Science*, **312**, 1637 (2006).
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PS-23 – Controlling photoinduced processes in supramolecular assemblies

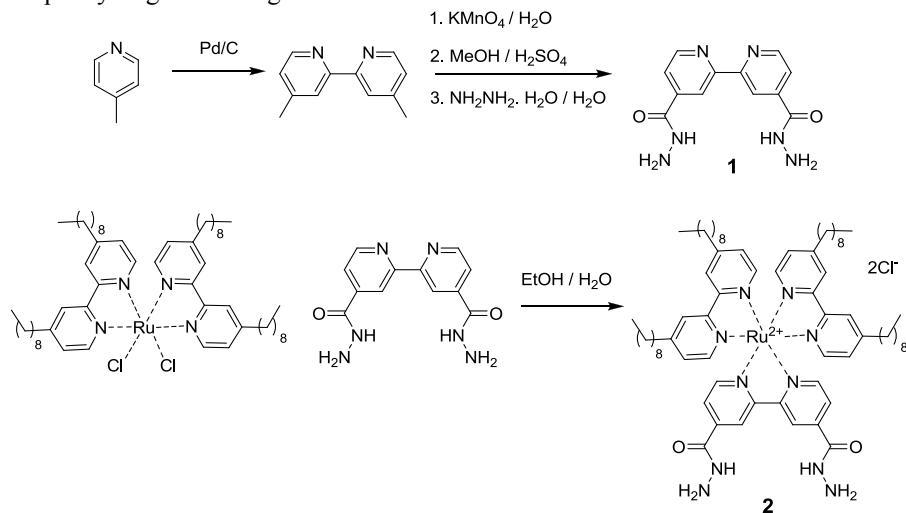
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¹ Dpto. Química Orgánica, Universidad de Málaga, 29071, Málaga, España

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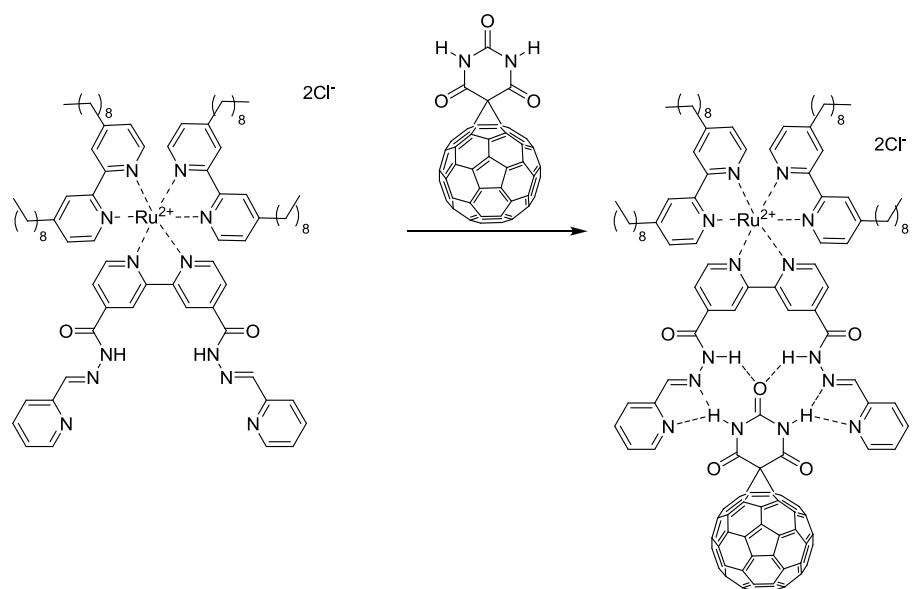
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A 2,2'-bipyridine derivative complex **1** incorporating two hydrazone substituents has been prepared and its binding to photo and electroactive metal ions such as Ru (II) has been explored. In order to obtain **2**, the hydrogen- bonding sites will be oriented in such a way so as to construct a molecular cavity suitable for binding barbituric acid derivatives through multiple hydrogen-bonding interactions:



Spectroscopic techniques (UV-vis absorption, fluorescence emission, NMR) have been used over a wide concentration range based on previous experience on related systems. Subsequently, the availability of barbituric acid derivatives possessing photoactive (eg pyrene) or electroactive substituents (such as fullerene C₆₀) will allow us to construct supramolecular donor-acceptor dyads in which allosteric effects are present [1].

It is expected that upon complexation of Ru (II), a suitable binding cavity for the barbituric acid moiety is formed, which will lead to binding of the C₆₀ derivative. This architecture will thus promote photoinduced electron y/o energy transfer quenching of the Ru (II) excited state. We can expect to observe highly efficient ultra-fast electron transfer from the Ru (II) metal center to the fullerene core due to optimal spatial distribution of the acceptor moieties [2].



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PS-24 – Influence of solvent polarity on the photophysical properties of naphthalene-based bichromophoric dyads

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A classical example of photoinduced electron transfer reaction is excited state interaction between aromatic chromophores and electron donor amines [1]. In addition, typical photoinduced reactions of naphthalene (NP) and its derivatives are electron transfer (et) or exciplex formation (ex) with appropriate partners such as amines. Wavelength-dependent stereodifferentiation has been observed in the fluorescence quenching of chiral dyads by triethylamine *via* exciplex formation [2]. On the other hand, we have recently reported photophysical and photochemical studies on Cinacalceut, a calcimimetic drug which contains a NP chromophore where intramolecular dynamic quenching attributed to exciplex formation was also observed [3].

In this context, novel diastereomeric dyads including two NP units connected by an amine spacer have been synthesized. These bichromophoric compounds are composed of (*S*-Naproxen (NPX) and (*R*)- or (*S*-1-(1-Naphthyl)-ethylamine (NEA) (Fig. 1).

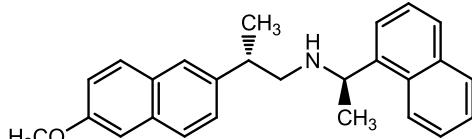


Figure 1. Structure of (*S,R*)-NPX-NEA

In the present work, the main goal is to perform a systematic characterization of the excited state behavior of the dyads in solvents with different polarities such as hexane, acetonitrile and tetrahydrofuran (THF).

Absorption spectra of NPX-NEA dyads, in different solvents, reflect the contribution of the two chromophoric units, and no significant differences were found in any of them.

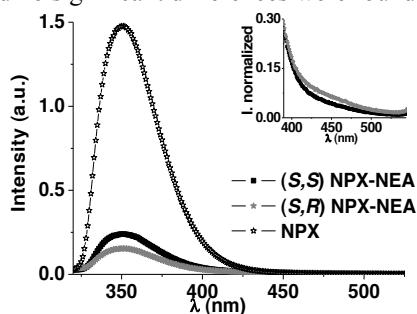


Figure 2. Emission spectra of NPX, (*S,R*)-NPX-NEA and (*S,S*)-NPX-NEA in acetonitrile ($\lambda_{\text{exc}} = 281$ nm) under nitrogen. The inset shows the amplified exciplex emission.

As shown in Figure 2, fluorescence spectrum ($\lambda_{\text{exc}} = 281 \text{ nm}$) of (*S,S*- and (*S,R*)-NPX-NEA showed an emission band with maximum at *ca.* 352 nm corresponding to NPX. Excited state interactions *via* electron transfer, exciplex formation or energy transfer may be favorable depending on solvent polarity. Thus, in all solvents under study (acetonitrile, THF and *n*-hexane) extensive singlet-singlet energy transfer from NEA to NPX occurs. However, an intramolecular quenching by the amino group was only observed in acetonitrile and THF; it can be attributed either to photoinduced electron transfer or to exciplex formation. These experimental observations are in good agreement with the ΔG values determined by the Rehm-Weller equations. In the case of THF only exciplex formation is energetically favorable while for acetonitrile both processes are possible.

Laser flash photolysis experiments ($\lambda_{\text{exc}} = 308 \text{ nm}$) revealed formation of the triplet excited state (Fig. 3A) with a maximum at 430 nm, which was efficiently quenched by oxygen. Kinetic analysis of the triplet decays is shown in figure 3B.

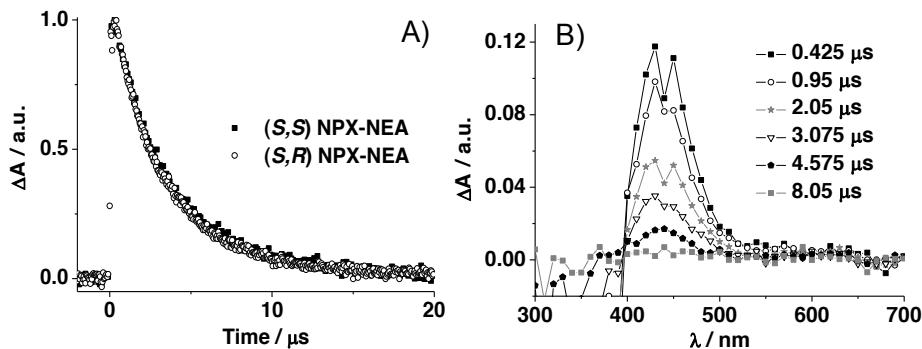


Figure 3. A) Spectra of (*S,R*)-NPX-NEA in acetonitrile obtained at different delay times after the laser pulse B) Decay traces monitored at 430 nm of (*S,S*- and (*S,R*)-NPX-NEA in acetonitrile.

Interestingly, intersystem crossing quantum yields of dyads were higher than expected, taking into account the intramolecular quenching of its singlet excited precursor. This suggests population of the triplet state by back electron transfer at the radical ion pair or by intersystem crossing at the exciplex.

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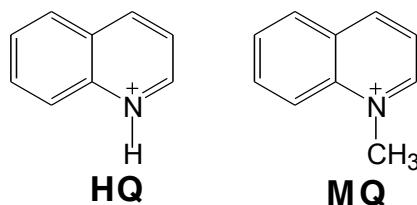
PS-25 – Excited-state proton-coupled electron transfer from alcohols and water to quinolinium cations

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Coupling of proton transfer and electron motion is an issue of great interest because of its crucial role in essential processes occurring in living systems, like photosynthesis, respiration or DNA chemical damage and repair [1].



Fluorescence from quinolinium cation, **HQ**, and derivatives is quenched by inorganic anions, typically halides, as a result of an electron transfer taking place from the anion to the excited cation [2]. In this work we have studied the influence of water, methanol, ethanol, 1-propanol, ethylene glycol and 1,3-propanediol on the fluorescence of **HQ** and **MQ** in acetonitrile. We have found that all these species quench the fluorescence of **HQ** and **MQ**. Whereas only one quencher molecule participates in the deactivation process by halides, two protic molecules are involved in the fluorescence quenching by water and alcohols. The efficiency of the process increased as the ionization potential of the quencher decreased for all the species investigated, this suggesting that an electron transfer from the quencher to **HQ^{*}** and **MQ^{*}** is involved in the deactivation process. Analysis of the steady-state and time-resolved fluorescence data led us to propose that an exciplex between **HQ^{*}** or **MQ^{*}** and one water or alcohol molecule is first formed, and upon arrival of a second quencher molecule, a proton-coupled electron transfer takes place.

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Acknowledgement. We thank the Spanish Ministry of Education and Science and the European Regional Development Fund (Grant CTQ2010-17835) and the Xunta de Galicia (Grant IN845B-2010/094) for financial support of our work.

PS-26 – Photoacid and photobasic properties of hydroxyphenylimidazo-pyridine derivatives. New ESIPT-TICT dyes showing very efficient radiationless deactivation

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The photoacid and photobasic properties of 2-(2'-hydroxyphenyl)imidazo[4,5-*b*]pyridine (**1**, Figure 1) and its methylated derivatives 2-(2'-methoxyphenyl)-imidazo[4,5-*b*]pyridine (**1-OMe**) and 2-(2'-hydroxyphenyl)-4-methylimidazo[4,5-*b*]pyridine (**1-NMe**) have been studied by UV-vis absorption spectroscopy, steady-state and time-resolved fluorescence spectroscopy.

The neutral forms of **1** and **1-NMe** mainly exist as planar *syn* normal forms, with the hydroxyl group hydrogen bonded to the benzimidazole N3. These *syn* normal forms of **1** and **1-NMe** undergo an ultrafast excited-state intramolecular proton transfer (ESIPT) to yield an excited tautomer. Protonation/methylation of the pyridine nitrogen enhances an intramolecular twisting of the tautomer associated with internal charge transfer (TICT) and subsequent very fast internal conversion in the excited state.

We have proved the strong photobasic properties of the pyridine nitrogen in these molecules by observing that a large fraction of **1-OMe** molecules gets protonated in the excited state in the acidic solvent trifluoroethanol.

In acidic media, an equilibrium between pyridinium and imidazolium cations in the ground state was found for **1** and **1-OMe**, the absorption and fluorescence spectra of the two cations being strongly overlapped. We devised a method to resolve the overlapping spectra by applying principal component global analysis to a series of excitation spectra taken at different monitoring emission wavenumbers. This procedure allowed us to resolve the components of the absorption and fluorescence spectra and estimate the equilibrium constant between the cations in several solvents.

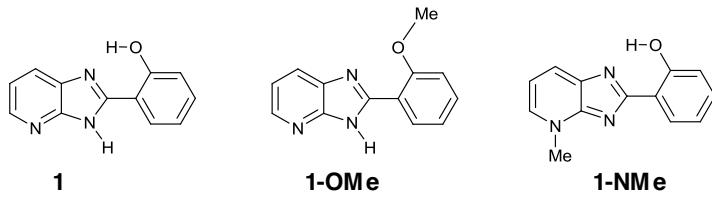


Figure 1. Molecular structure of the compounds studied in this work.

Acknowledgement. We are indebted to the Spanish Ministry of Education and Science and the European Regional Development Fund (Grant CTQ2010-17835) and the Xunta de Galicia (Grant IN845B-2010/094) for financial support of our work.

PS-27 – Revisiting Maya Blue with Indigo and Thioindigo

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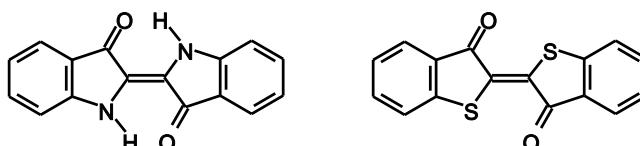
The ancient Maya civilization developed what can be considered the first organic/inorganic hybrid consisting of a dye (indigo) and a clay (attapulgite), which has become known as Maya Blue. Due to its attractive turquoise colour and light fastness, Maya blue was widely used in mural paintings, ceramics, codices [1].

Maya Blue has a unique color and stability that can be explained with a model where indigo dye fills the grooves present at the surface of the clay, forming a hydrogen bonded organic/inorganic complex [1]. This incorporation protects the organic dye, leading to outstanding stability which has made possible the preservation of the colour for centuries in paintings submitted to severe environmental conditions, in particular those involving light (photodegradation). The high stability of Maya Blue was further tested in laboratory where this hybrid was found resistant to several oxidizing and reducing agents, organic solvents, strong acids and alkaline, and high temperatures.

Indigo was the blue colour used by almost all the ancient civilizations and one of the first natural molecules to be synthetically produced (L. von Bayer), thus paving the way to the modern chemical industry. The longevity of indigo is chemically related to its high stability towards light (photostability). Indeed, besides its unique color, its remarkable stability has been linked to inefficient fluorescence and intersystem crossing processes, a low triplet energy and fast $S_1 \rightsquigarrow S_0$ (and highly efficient) radiationless internal conversion channel with a value of 99.99% [3,4]. Moreover, the deactivation of the excited state of indigo has been linked to a process resulting from fast intramolecular hydrogen-bonding between the two adjacent carbonyl and N-H groups [2,3,5].

The contribution of indigo in MB and thioindigo (in a modified version of this hybrid) was further investigated by optical and fluorescence spectroscopy in solution and in the solid state. With indigo, it was found that dehydroindigo plays a role in the formation and final structure (and therefore color) of this pigment [2].

In the case of thioindigo, the absence of proton transfer leads to completely different photophysical properties, with high fluorescence and intersystem crossing yields. This allows to obtain further information on the location and stability of the resultant hybrid by steady-state and time-resolved fluorescence techniques.



Indigo

Thioindigo

Figure 1. Structures of indigo and thiondigo

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The overall spectral and photophysical properties of indigo and thioindigo when incorporated with sepiolite and attapulgite clays will be presented and discussed aiming to contribute to the elucidation of this puzzling hybrid.

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Acknowledgement: We are grateful to POCI (Project PTDC/QUI-QUI/099388/2008), FCT and FEDER for further funding Raquel Rondão acknowledges FCT for a PhD grant (SFRH/BD/38882/2007).

PS-28 – Photochemical and photophysical studies on dipicolinic acid and its photoproducts

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Dipicolinic acid (pyridine-2,6-dicarboxylic acid, DPA) is an endogenous compound of bacterial spores. In the literature, it has been suggested that it plays a key role in the formation of spore photoproduct (namely 5-thyminyl-5,6-dihydrothymine, SP) [1,2].

In fact, decrease of SP formation yield has been observed in spore mutants lacking DPA. Photosensitizing properties of DPA have been further supported by studies in less complex media like isolated DNA, TpT dinucleotides or thymidine. Indeed, irradiation of DNA dry films in the presence of DPA has shown the increase of SP. Interestingly, cyclobutane pyrimidine dimers (Thy \leftrightarrow Thy, and to a lesser extent Thy \leftrightarrow Cyt and Cyt \leftrightarrow Thy) have also been detected. Thus, the available data are in agreement with the role of DPA as triplet photosensitizer, acting as donor in a triplet-triplet energy transfer process [3-6].

The aim of this study was to establish the photophysical properties of DPA and to elucidate the mechanism of SP formation. However, the high photolability of DPA in aqueous solution, due to decarboxylation, made an accurate characterization difficult. This problem has been avoided by studying its stable dimethyl ester (DMDPA). Phosphorescence study allowed detection of the triplet excited state of DMDPA (${}^3\text{DMDPA}^*$), which exhibits an emission centered at 400 nm (triplet excited state energy of *ca.* 76 kcal \times mol $^{-1}$) supporting the possibility of a triplet-triplet energy transfer from ${}^3\text{DMDPA}^*$ (or ${}^3\text{DPA}^*$) to thymidine. Laser flash photolysis experiments revealed a transient absorption at $\lambda_{\text{max}} = 300$ nm, which was assigned to ${}^3\text{DMDPA}^*$ by quenching experiments. Moreover, an efficient quenching of ${}^3\text{DMDPA}^*$ by thymidine was observed as the result of a triplet-triplet energy transfer. This result is in agreement with the potential role of DPA as photosensitizer of dimeric pyrimidine lesion.

Finally, a similar study was performed on DPA photoproducts to investigate their photosensitizing properties.

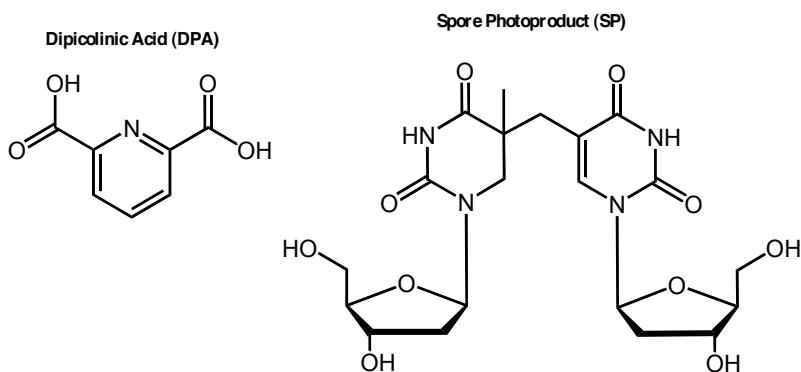


Figure 1. Structures of dipicolinic acid and spore photoproduct

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PS-29 – Photogeneration and photosensitizing action of humic substances in the presence of riboflavin. A kinetic and mechanistic study

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Humic substances are mixtures of organic compounds abundant in terrestrial and aquatic systems [1], and humic acids (HAs) are the predominant compounds in these mixtures. The available evidence indicates that these substances should be generated through the oxidative natural degradation/photodegradation of polyphenolic materials by complex thermal and photochemical mechanisms. In order to advance in the study of these mechanisms, the present contribution discusses: (a) the kinetic and mechanistic aspects of the photoprocesses that operate in the photodegradation of gallic acid (GA) –a polyphenol naturally formed after lignin degradation– under conditions frequently found in nature, i.e. aqueous environment, visible-light illumination and sensitization with riboflavin (Rf, vitamin B₂) –a native photosensitizer present as traces in waters of rivers, lakes and seas [2]–; and (b) the photosensitizing properties of mixtures Rf + HAs in the photodegradation of phenolic water-contaminants, using phenol (PhOH) and 3-hydroxypyridine (3-OHP) as models. Both, Rf and HAs, have been considered to individually play important roles in the photochemical degradation of organic materials in nature [3,4].

In pH 7 aqueous solution and in the presence of Rf, the results indicate that GA is photodegraded through relatively fast processes, with the involvement of the species singlet molecular oxygen ($O_2(^1\Delta_g)$), superoxide radical anion ($O_2^{\cdot -}$), and hydrogen peroxide (H_2O_2), all of them photogenerated from triplet excited Rf. This indicates that in natural waters GA can undergo spontaneous photodegradation under environmental conditions, and that radical species generated in the presence of Rf can participate in condensation and/or polymerization reactions promoting the natural synthesis of humic substances.

In parallel, other systematic experiments have shown that the mixture Rf + HAs photogenerates $O_2(^1\Delta_g)$ and $O_2^{\cdot -}$, and that the generation of the latter is favoured in the presence of electron donors such as hydroxyaromatic compounds. Taken the rate of oxygen consumption as a measure of the overall oxidation rate of each substrate model compound, it can be deduced that the photooxidation of 3-OHP at pH 7, sensitizing with low Rf and HAs concentrations, is an efficient process, if compared with the photooxidation rate of the known oxidizable target furfuryl alcohol. PhOH is only photodegraded in alkaline aqueous solutions.

Using the mixture Rf + HAs as photosensitizer, it was also observed that the rate of oxygen consumption by 3-OHP was lower than the simple addition of the oxygen uptake rates for the separated photooxidations of 3-OHP with Rf or HAs. This result has been attributed to a

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catalytic decomposition of O_2^- by HAs, which competes with 3-OHP by this oxidative species, inhibiting at the same time the oxygen-consumer channel, especially active in the presence of 3-OHP.

In natural waters with a relatively high local concentration of contaminants and a comparatively low concentration of photosensitizers, the former kinetic evaluations suggest that the phenolic contaminants can be degraded, mainly through oxidative reactions, appearing at the same time a simultaneous photoprotective effect against bleaching of the sensitizers.

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PS-30 – Femto to millisecond studies of indole-based squaraines molecules in solution

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The femto-to-millisecond dynamics of five types of indole-based squaraines (SQs) molecules [1-3] in solution have been studied.

Steady-state UV-vis absorption and emission spectra are narrow, with a Stokes shift of about 300 cm^{-1} . Time-resolved picosecond experiments gave two lifetimes (with values between $\tau_1=70\text{-}210 \text{ ps}$ and $\tau_2=290\text{-}540 \text{ ps}$ in acetonitrile for the five studied SQs) that have been assigned to two possible stereoisomers in the ground state in *trans* configuration. Experiments with solvents of different polarity and viscosity were performed to probe the twisting relaxation of the S_1 state. In SQ 41, lifetimes of 1.72, 0.46 and 0.29 ns were determined for the longer component in triacetin, dichloromethane and acetonitrile, respectively. This reflects the stronger quenching of the S_1 state in highly polar and low viscous solvents.

Nanosecond flash photolysis experiments showed the transient signals of the *cis* photoisomer that is formed after the twisting process of S_1 . The relaxation of this transient signal follows the *cis-trans* back photoisomerization, recovering the initial ground state of the SQs. Lifetimes of 4.0, 3.0 and 1.6, μs , for SQ 41 were obtained from the fits in triacetin, acetonitrile and dichloromethane, respectively.

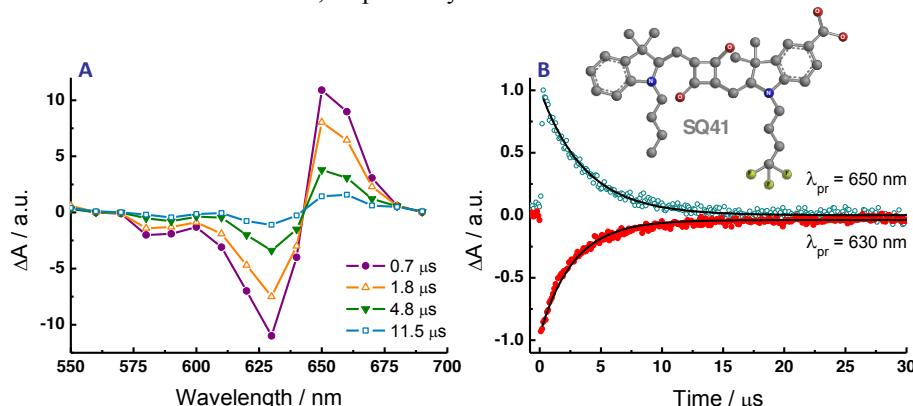


Figure 1. **A:** Nanosecond transient absorption spectra of SQ 41 in acetonitrile at four different time delays. **B:** Time profiles of the same sample observed at 650 and 630 nm and best fits of the experimental data. Insert: Molecular structure of the asymmetric SQ41.

The femtosecond transient absorption results showed a 70 fs fast component which is to a large extent independent on the used solvent and on the type of SQs. This component presents as a rise at the maximum of the transient signal or as a decay at the blue-side of the spectrum, producing a net narrowing of the peak. We attribute this event to an intramolecular vibrational-energy relaxation (IVR) process. In the longer time scale, two lifetimes are necessary to fit the data, with values between $\tau_1=55-75$ ps and $\tau_2=230-705$ ps in acetonitrile for the studied SQs. These numbers are in good agreement with the previously reported lifetimes from the picosecond experiments.

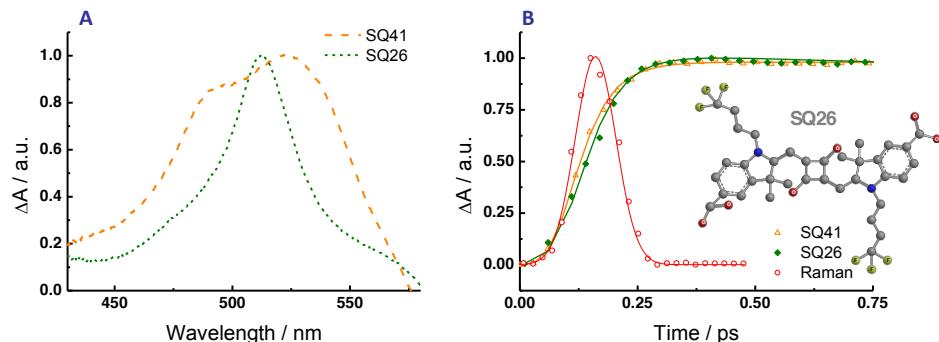


Figure 2. **A:** Normalized femtosecond transient absorption spectra of the asymmetric SQ41 and the symmetric SQ26 in acetonitrile solvent at 1 ps after the laser pump pulse. **B:** Time profiles of the signals probed near to the maximum of transient absorption band with the best fits of the experimental data. Raman peak of the ACN solvent is shown. Insert: Molecular structure of the symmetric SQ26.

In conclusion, the S_1 state of SQs presents a non-radiative deactivating pathway consisting in a twisting process with a potential energy barrier E_b . As expected, viscous solvents produce an increase in E_b . We have been able to observe the signal of the *cis* stereoisomer and to follow the kinetic process of the back reaction to the *trans* photoisomer in the nanosecond time scale. Three lifetimes were obtained in the femtosecond experiments. The shortest one has been assigned to an IVR process. The longer ones match with those obtained in picosecond experiments and they can be explained taking into account two stereoisomers in the ground state.

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PS-31 – Photocatalytic degradation of Diclofenac and Carbamazepine in aqueous solution

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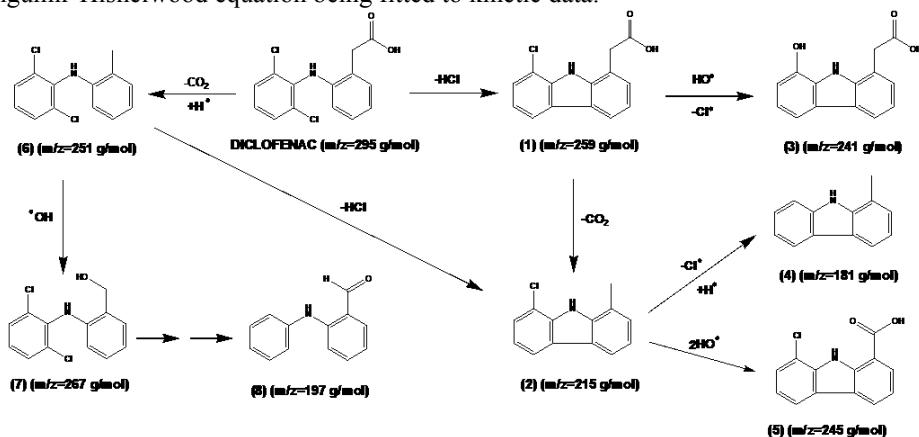
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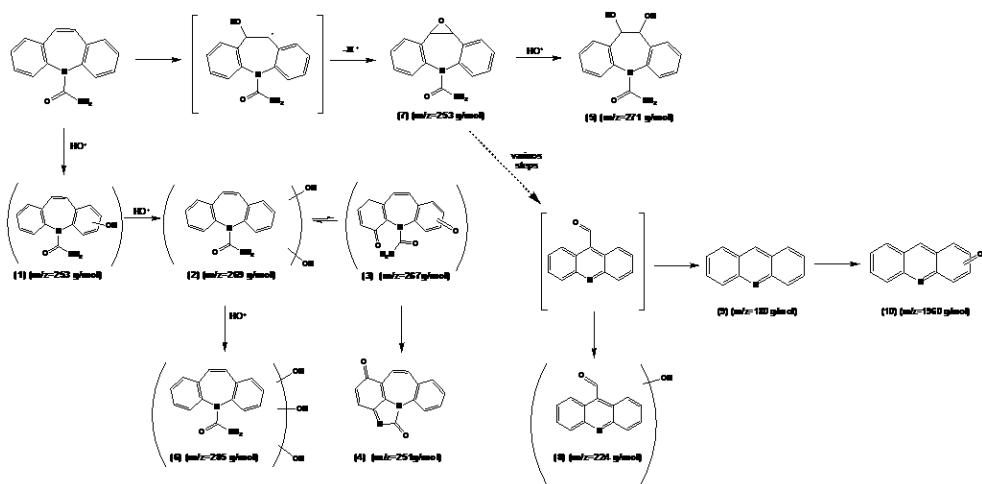
Diclofenac (DIC), 2-[2', 6'-(dichlorophenyl)amino]phenylacetic acid, the active principle of the well-known Voltaren®, is a non-steroidal anti-inflammatory drug (NSAID) used to treat inflammation and pain associated with different rheumatic and non-rheumatic diseases [1]. Carbamazepine (CBZ), 5H-dibenzo[b,f]azepine-5-carboxamide, is a dibenzazepine derivative used to control some types of seizures in treatment of different relevant psychiatric disorders [2], which has been found in 70% of the samples analyzed. in different rivers around Madrid [3].

Toxicity studies point out that DIC show adverse effects even at low concentrations [4,5], like cytotoxicity to liver, kidney and gill cells, as well as renal lesions; whereas CBZ has been evaluated as dangerous for aquatic life, including bacteria, algae, invertebrate, and fish [6].

We investigated the kinetics of the photocatalytic degradation of DIC and CBZ under near UV-Vis and UV irradiation using TiO₂ P25, synthesized TiO₂ (anatase and rutile), and composites of oxidized-multi-walled-carbon-nanotube: anatase as catalysts. The optimal conditions were obtained by changing factors relevant to the kinetics, such as the type and load of catalyst, presence of dissolved O₂, and addition of co-oxidants like H₂O₂. Experimental conditions were designed to work under apparent first order conditions; Langumir-Hishelwood equation being fitted to kinetic data.



Scheme 1. Proposed photocatalytic degradation mechanism of DIC in aqueous solution



Scheme 2. Proposed photocatalytic degradation mechanism of CBZ in aqueous solution

Both pharmaceuticals undergo photodegradation, the rate constant being *ca.* 0.9 and 0.3 min^{-1} for DIC and CBZ, respectively, at the optimal conditions (0.5 g/L of synthesized anatase and 50% O_2 (v/v) under UV irradiation, and 0.5 g/L of P25, 5mM of H_2O_2 under anaerobic conditions when using NUV-Vis light).

We have identified photoproducts and some reaction intermediates by using HPLC with MS detection.

The proposed degradation mechanism [7, 8] for Diclofenac and Carbamazepine in aqueous solution is shown in Scheme 1 and 2, respectively.

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**PS-33 – Adsorption and photocatalytic degradation of
2,4-dichlorophenol on TiO₂ and ZnO**

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The photocatalytic degradation and mineralization of 2,4-dichlorophenol (2,4-DP) with TiO₂ (Degussa P-25) and ZnO (Aldrich) at different pHs and catalyst loadings has been studied. Optimal conditions are pH₀ 5 and 2g·L⁻¹ and pH₀ 7 and 2g·L⁻¹ for TiO₂ and ZnO respectively. In spite of the fact that the kinetic of degradation is much faster for ZnO, $k = 0.022 \text{ ppm}\cdot\text{s}^{-1}$ vs. $k = 0.038 \text{ ppm}\cdot\text{s}^{-1}$, the degradation using ZnO has two outstanding drawbacks: slower mineralization and releasing of Zn²⁺ to the bulk solution. Dissolved zinc concentration is not only due to catalyst solubility and catalyst photocorrosion but also to extraction by the substrate so that the maximum Zn²⁺ concentration is reached just when 2,4-DP disappears completely from the dissolution (Figure 1). From the application of Langmuir-Hishelwood kinetic model, the adsorption constants are also obtained. It is observed that the adsorption constant in TiO₂ is greater than in ZnO. This is in accordance with FTIR results that show that 2,4-DP molecule interacts stronger with the ZnO surface than with the TiO₂ one although in both cases, the 2,4-DP interaction is by means of the formation of a phenolate.

In order to improve the degradation of 2,4-DP with TiO₂, different oxidants were added. The three oxidants tried were ozone, hydrogen peroxide and sodium peroxydisulfate. All of them are able to reduce the pollutant in presence only of light. However, in heterogeneous photocatalysis, the effect of these oxidants would not be justified, as hydrogen peroxide and ozone improve only slightly the degradation and mineralization of 2,4-DP, while sodium disulphate inhibits both processes.

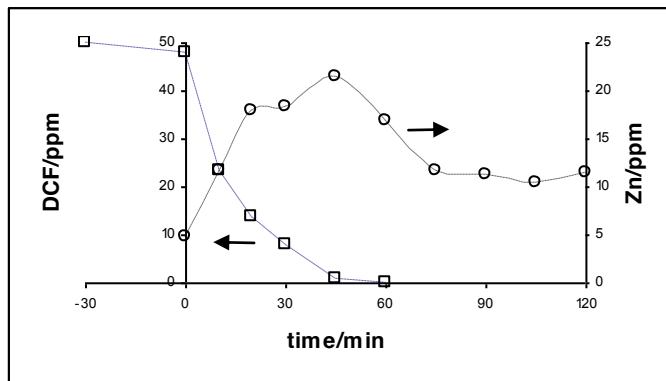


Figure 1. Degradation of 50 ppm of 2,4-DP in the presence of 2 g·L⁻¹ of ZnO, pH₀ = 7: (□) concentration of 2,4-DP and (○) total concentration of Zn.

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PS-34 – Improved photoefficiency of TiO₂ based films with carbon nanotubes on the degradation of aqueous caffeine

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One of the most active areas in heterogeneous photocatalysis has been the application to environmental cleanup. Titanium dioxide (TiO₂) is considered the catalyst of excellence in many photocatalysis applications, including the degradation of organic pollutants [1]. Recent works have emphasized the higher efficiency of titanium dioxide/carbon nanotubes nanostructured composites (TiO₂/CNT) in heterogeneous photocatalytic applications [2].

Although TiO₂ particles in aqueous suspension present a high photocatalytic activity for many pollutants, the post-separation step of suspended powders, typically required in slurry operation, is tedious and expensive. This can be avoided by immobilizing the active photocatalyst [3].

In the present work, two nanocrystalline TiO₂ samples (TiO₂ from Sigma Aldrich, “SA” and P25 from Evonik, “EP”) were immobilized as thin films in glass slides by using the doctor blade technique. TiO₂/CNT composite films were prepared by the same technique with a TiO₂:CNT mass ratio of 5:1. The photocatalytic experiments were performed in a glass cylindrical reactor filled with 7.5 mL of caffeine aqueous solutions (50 mg L⁻¹). The illuminated area on the films was kept at 0.79 cm², using near-UV to visible ($\lambda > 366$ nm) radiation. Fig. 1 shows the results obtained for caffeine degradation normalized per mass fraction of TiO₂ (y_{TiO_2}).

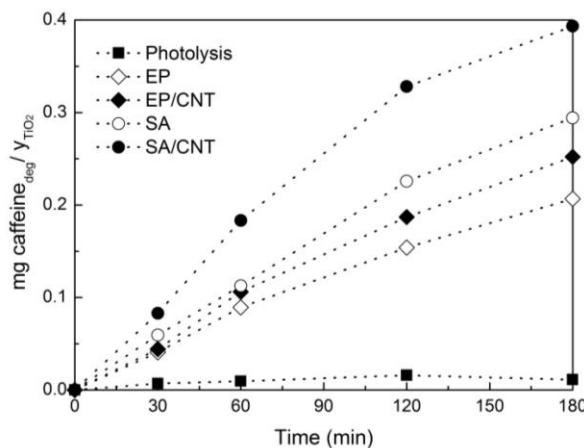


Figure 1. Evolution of caffeine degradation during photolysis and photocatalytic reactions using TiO₂ and TiO₂/CNT films.

In the applied conditions, caffeine is resistant to photolysis and is photocatalytically degraded in the presence of bare TiO₂ and TiO₂/CNT composite films. The photoefficiency of the immobilized catalysts appear to be related to the inherent properties of the materials and to the characteristics of the resulting films. SA-containing films show higher efficiency for the photocatalytic degradation of caffeine than EP-based ones, which is attributed to the physical-chemical and optical properties of these materials, such as TiO₂ anatase content and TiO₂ particle size. Among the materials tested the best efficiency was observed for SA/CNT, which can be also attributed to the high homogeneity of the film produced with this catalyst, as shown in Fig. 2.

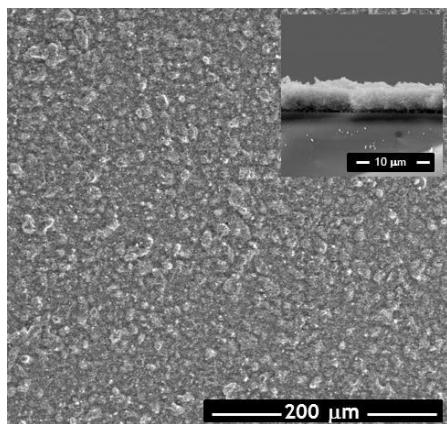


Figure 2. SEM image of SA/CNT

Caffeine photodegradation was improved by the use of TiO₂/CNT composites. This increase in the photoefficiency is attributed to the creation of an electronic interphase interaction between CNT and TiO₂ phases, which leads to a decrease in the bandgap energy of the composite material.

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PS-35 – Large area nanoarrays made by interference lithography

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During the last decades, the evolution of both fabrication and characterization techniques has allowed the development of Nanotechnology. Specifically arrays of nanostructured magnets have been continuously developed due to their potential applications to high density data storage devices and magnetic memories. These systems are also ideal candidates for the study of magnetic phenomena at sub-micron length scales [1,2].

Controlling the material properties, such as crystalline lattice, chemical composition, sample size, thickness, shape and distance between elements, the magnetic behaviour could be tailored [3]. Our work is focused on the preparation and study of nanostructured systems as a function of the material properties. To carry out this proposal, a combination of Interference Lithography system, Sputtering methods and chemical processes or lift-off of the mask are the used experimental nanofabrication techniques.

The interference lithography (IL) system works with a continuous He:Cd laser at $\lambda=325\text{nm}$. Interference lithography allows creating large area arrays of periodic elements, in short times and with relative easy equipment [4]. The IL processing has various related subprocesses, such as the spin coating of a photosensitive resist layer, the exposure to a selected wavelength and a development step.

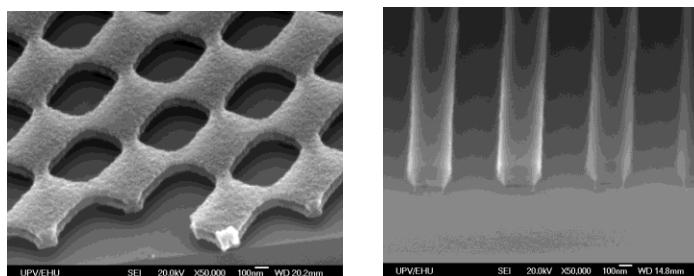


Figure 1. Scanning Electron Microscopy images of periodic patterns made by interference lithography

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PS-36 – Porphyrin Sensitized Solar Cells Performance Dependence on Dye Properties and Dye-Semiconductor Anchoring Mode and Distance

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TiO₂ nanocrystalline ruthenium polypyridyl Dye-Sensitized Solar Cells (DSSCs) are alternative and very promising devices for solar energy conversion [1]. However, these devices still present low efficiencies (11%) and high cost. Therefore, research efforts focussed toward finding organic-based dyes that avoid the use of noble metals are valuable. Porphyrins and metalloporphyrins are particularly attractive dyes attending to their primary role in photosynthesis. Furthermore, porphyrins can be easily derivatized with different substituents and metals in order to enhance their affinity and distance to TiO₂ as well as their redox and spectroscopic properties [2]. These extremely versatile organic dyes are both useful for the understanding of the individual steps involved in energy conversion in DSSCs and for ultimate economical efficient application.

Our aim is to achieve the basis of knowledge in order to do a rational design of tetrapyrrolic macrocycles dyes and their metal complexes for DSSC. For this study a restricted number of porphyrins were chosen and synthesized. We used a carboxylic group to anchor the dye into the TiO₂. Distinct distance and positions of the anchoring group were studied. The central metal was changed. Dye photophysical and electrochemical studies have been done. The DSSC performance was accessed by measuring the IPCE profiles and I-V curves, yielding their IPCE, V_{OC}, J_{SC} and η values. Solar cell performances are rationalized in terms of the photophysical and electrochemical properties of the porphyrins, and in terms of adsorption mode and distance.

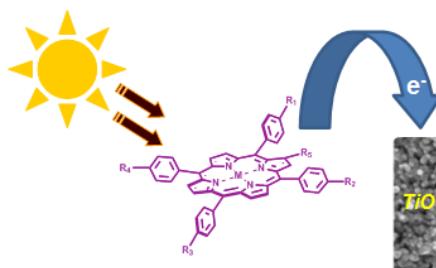


Figure 1. Electron injection from an excited porphyrin to TiO₂.

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Acknowledgement: We thank FCT and FEDER for financial support and a grant to P. Jesus through project PTDC/QUI/70637/2006. CJPM thanks FCT for PhD grant BD/37652/2007.

PS-37 – Fluorescent hybrid silica nanoparticles incorporating perylenediimide derivatives in the framework

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Perylene dyes are highly versatile molecules due to their high chemical, thermal and photochemical stability, high molar absorptivities in the visible wavelengths, and high fluorescence quantum yields. Besides these outstanding properties, perylene dyes also offer wide possibilities for chemical functionalization via the introduction of substituents in the peri and bay positions. This derivatization can efficiently tune the properties of the perylene dyes for applications, such as solar cells, lasers, single molecule spectroscopy, imaging, bioanalysis, and photoactive materials [1].

Silica nanoparticles (SiNP) obtained by the Stöber method have been extensively studied and their characteristics can be tuned during the synthesis to obtain a wide range of particle diameters (20-500 nm) and to incorporate molecules such as catalysts, drugs, inorganic complexes, or fluorophores [2]. These molecules can be physically entrapped inside the core [2] or covalently attached to the silica network during the synthesis procedure, using the same strategy as for periodic mesoporous organosilicas [3]. Alternatively, the surface of SiNP can be functionalized postsynthesis with organic alkoxy silane compounds for covalent immobilization or adsorption of molecules and biomolecules or to allow the synthesis of a polymer, metal, or inorganic shell.

Mesoporous silica nanoparticles [4] with well-defined and controllable particle morphology are exceptional supports for molecules and polymers that have a tendency to aggregate, forming dimers or aggregates with less desirable properties. Molecules with two or more trialkoxysilane peripheral groups can be incorporated in the silica framework during the synthesis of the nanoparticles (following the same strategy used for the PMOs), with a high level of dispersion. After template removal, the pore is available for solvent diffusion or to accommodate polymers or other entities [4].

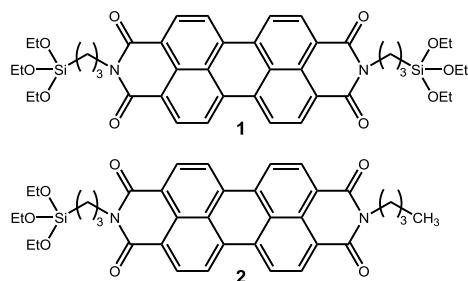


Figure 1. Structure of Perylenediimide derivatives bearing one or two alkoxy silane groups.

Here we describe the preparation of silica nanoparticles with hexagonal arranged mesopores through a sol-gel process using a co-solvent, with perylenediimide derivative **1** (Figure 1) incorporated on the walls of the mesoporous structure. Different templates and co-solvents are used to obtain nanoparticles with different structural characteristics. The as-synthesized hybrid nanoparticles (before and after template removal) are characterized by powder XRD, isothermal gas adsorption and TEM. The photophysical properties (fluorescence excitation, emission and lifetime) of the perylenediimide derivatives will also be studied, and compared with those of perylenediimide derivatives **1** and **2** immobilized in silica nanoparticles (SiNPs) produced through the Stöber method (Figure 2) [5].

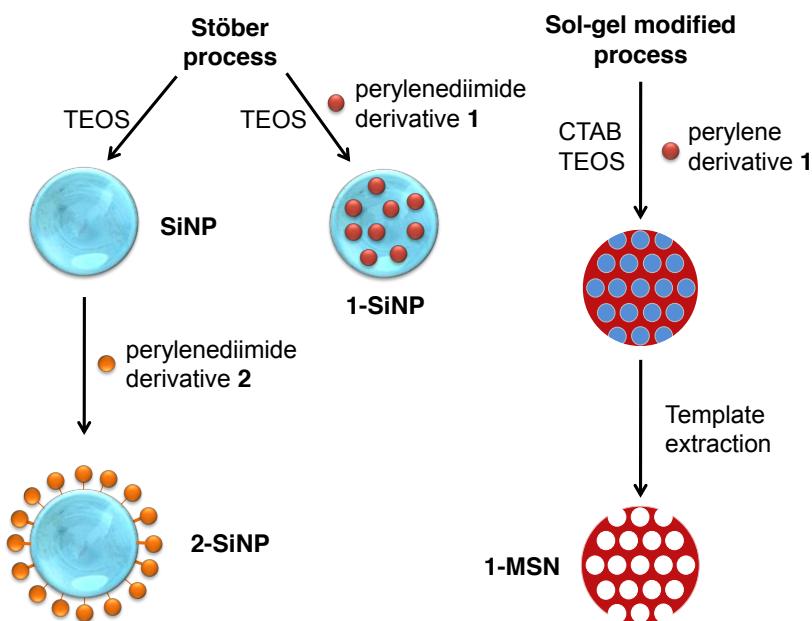


Figure 2. Silica Nanoparticles (SiNP) labeled with Perylenediimide **2** on the surface and Perylenediimide **1** inside the core; Mesoporous Silica Nanoparticles (MSN) with Perylenediimide **1** incorporated on the walls.

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Acknowledgement. This work was supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER) within projects PTDC/CTM/101627/2008 and PDCT/CTM/68451/2006.

PS-38 – Fluorescent silica-gold nanoparticles

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Gold nanoparticles have been observed to either enhance or quench the fluorescence emission of nearby dyes, depending on the orientation of the dye and its distance to the metal. Here we used a silica spacer shell to control the separation distance between fluorescent dyes and gold nanoparticles. Silica coating also improves the stability of gold nanoparticles and allows us to use well known procedures to incorporate the hybrid particles into polymer lattices or transferring them into polar and non-polar solvents.

Monodisperse citrate-stabilized gold nanoparticles obtained by a two-step reaction and transferred to ethanol using a thiol-ended methoxy-poly(ethylene glycol) (mPEG SH) [1], where coated with a silica shell by the Stöber method (Figure 1).

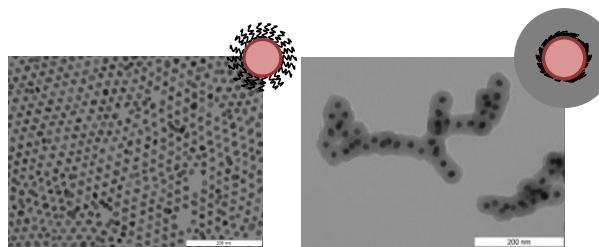


Figure 1. TEM images (scale bar 200 nm) of mPEG SH stabilized gold nanoparticles with 17 nm diameter (*left*) and the same particles with a 15 nm thick silica shell (*right*).

The hybrid nanoparticles were used to covalently link different perylenediimide dyes [2] in order to study the interaction between the gold core and the silica bound dye as a function of the dye transition dipole orientation relative to the gold surface (figure 2) [3].

The obtained fluorescently labeled hybrid nanoparticles show great potential for application in the fields of medical diagnostics, imaging, etc.

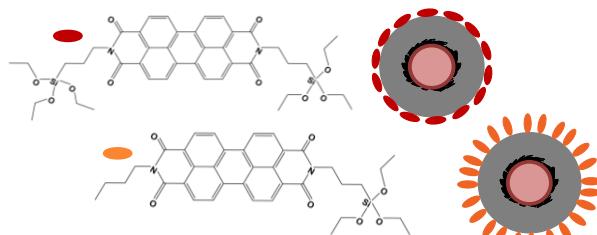


Figure 2. Perylenediimide derivatives covalently linked to the silica-gold nanoparticles.

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Acknowledgement. This work was supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER) within project PDCT/CTM/68451/2006.

PS-39 – Photoluminescence of core-shell quantum dots stabilized in water with a peptidomimetic gemini surfactant

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Semiconductor nanocrystals (quantum dots, QDs) have found numerous applications as fluorescent bioprobes due to their narrow emission bands, size-dependent tunability and resistance to photobleaching [1]. One of the main challenges for the biological application of QDs is the synthesis of water-soluble derivatives. Two main strategies are usually followed to prepare water soluble quantum dots: ligand exchange and encapsulation. The first strategy implies replacement of the hydrophobic ligands by hydrophilic ones imparting water solubility [2]. The second strategy consists in the encapsulation of the hydrophobic QDs with a protective shell of a hydrophilic material. Silica and hydrophilic polymers have been investigated as wrapping materials for this purpose [3]. In the case of polymeric materials, one well-established mechanism is the interdigitation of chains between the inner hydrophobic ligand and the outer hydrophilic polymer [4]. However, the use of low molecular weight molecules utilizing this intercalation mechanism has been less investigated [5].

In this work, we investigated the capability of peptidomimetic gemini surfactant **1a** to transfer commercial hydrophobic core-shell QDs to pure water (Figure 1). Compound **1a** could intercalate its long alkyl chains into the hexadecylamine ligands. The pseudopeptidic part of the compound along with the amine present in the bridge could impart the aqueous solubility to the system. The solubilised QDs have been characterized by steady-state and time resolved fluorimetry, FT-IR and transmission electron microscopy. The long fluorescence lifetime in water and the resistance to dynamic quenching by chloride ions are the most remarkable features of this new type of nanomaterials.

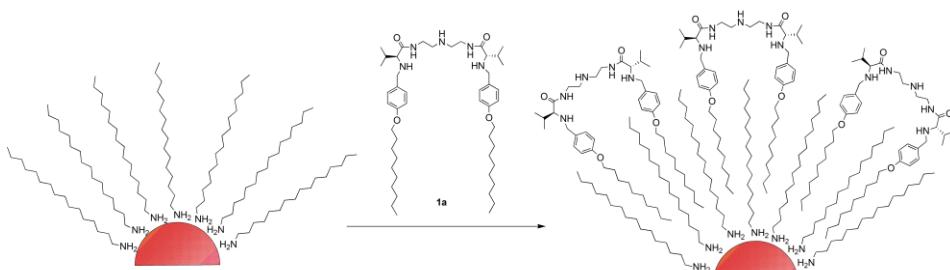


Figure 1. Schematic representation of the possible interdigitation process occurring between the hydrophobic ligands of the QDs and the alkyl chains of the peptidomimetic compound **1a**.

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Acknowledgement. Financial support from Spanish MICINN (CTQ2008-02907-E, CTQ2009-09953 and CTQ2009-14366-C02-01), GV (ACOMP/2010/258, ACOMP/2010/282), Fundació Caixa Castelló-UJI (project P1-1B-2009-59, P1-1B2009-58) is acknowledged. J. R. thanks MICINN (FPU fellowship).

PS-40 – Polymer - Quantum dot composites as supported fluorescent sensors for gaseous nitric oxide.

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Nitric oxide (NO) is a compound involved in the regulation of several physiological and pathophysiological mechanisms in the cardiovascular, central nervous and immune systems. This is associated to its role as intracellular and intercellular messenger [1]. Besides, NO and the other nitrogen oxides (NO_x) are considered major air pollutants and greenhouse gases [2].

During the last decade the importance of quantum dots (QDs) has increased because these inorganic nanocrystals have many photophysical, analytical, and biological applications. The use of QDs as fluorescent probes is widely used in different areas such as Medicine, Chemistry, Biology or Engineering. The main reason for their implementation is that QDs are able to overcome many of the limitations that have the organic fluorophores or fluorescent proteins. Furthermore, QDs have properties such as broad absorption and narrow emission spectra, high quantum yields, long fluorescence lifetimes and high photostability [3].

One of the most widely used quantum dots consists of a CdSe core and a ZnS shell which plays a protector role. Some very recent studies made with CdSe/ZnS QDs show that they are sensitive to nitric oxide (NO), which can induce a variation in their fluorescence signal [4].

On the other hand, numerous studies have been reported dealing with preparation of organic matrices with potential use in fluorescence analysis. One of the most usual approaches is to encapsulate a fluorescent probe in a polymer matrix [5]. A solid support is required because these devices increase the advantages over soluble systems, especially in gas phase analyses [6].

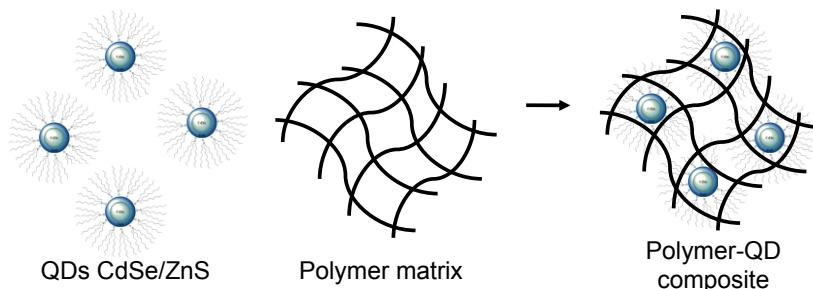


Figure 1. Adsorption process of QDs in polymer matrix in order to make a polymer – QD composite.

Our research group has developed recently some hydrophilic polymers based in poly-(2-hydroxyethyl methacrylate) (polyHEMA). Several chromophores have been embedded into the polymeric matrix displaying analytical applications as nitric oxide biosensors [7]. So far, the response and the sensitivity have been studied in aqueous and physiological media, but not in the gas phase. Therefore, in this work we explore the use of the polymer - QD composites as sensors of NO (g).

For this purpose we have proceeded to support the QDs on a series of hydrophilic polymers via surface adsorption. We have synthesized four different polymers - QDs. In all of them, the maximum emission is shifted to longer wavelengths compared to QDs in the original toluene solution. Subsequently we have evaluated the analytical response (fluorescence at 530 nm) to NO (g) at various concentrations. The detection limits for the analysis of NO have been estimated. This can be found around 0,1 ppm of NO.

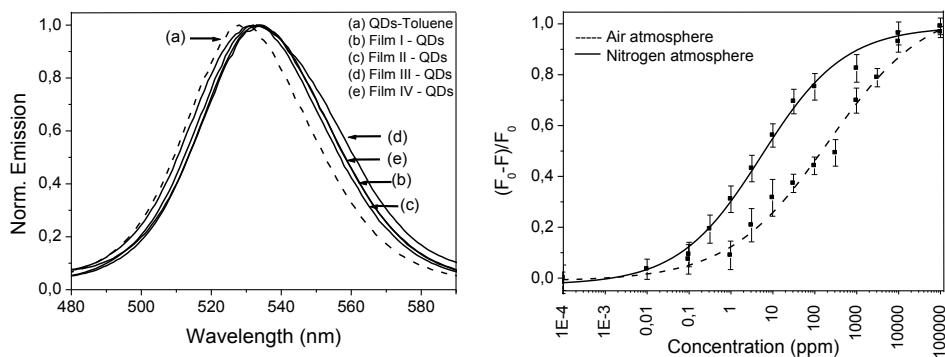


Figure 2. Left: emission spectra of QDs in a series of polymethacrylic matrices and toluene solution. Right: change of Film I-QDs emission signal in presence of nitric oxide in air and nitrogen atmosphere.

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PS-41 – Fluorescence Sensitivity towards Nitric Oxide displayed by Novel Organogel-Quantum Dot Hybrid Materials

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Organogels doped with fluorescent nanoparticles have attracted recent interest [1]. We have investigated further this topic by using a pseudopeptidic macrocycle (as organogelator) from our own research [2] and commercial core-shell CdSe/ZnS fluorescent quantum dots.

The new semisolid materials present the same excellent optical transparency and better thermal stability than the parent organogels without nanoparticles, but with the advantage of being fluorescent due to the presence of embedded semiconductor nanocrystals. The fluorescence lifetime of this kind of QD-organogel hybrid materials is reported for the first time and it has been found to be similar to the lifetime of QDs in solution (toluene).

The chemical sensing ability of the hybrid organogels towards diluted gaseous nitric oxide (NO) has been investigated by steady-state fluorescence spectroscopy. The fluorescence of the organogels is quenched by NO with a linear response for concentrations of NO from 0.5 to 5 ppm.

In Figure 1 it is depicted a model for the interaction of the studied quantum dots with the fibres of the self-assembled organogelator.

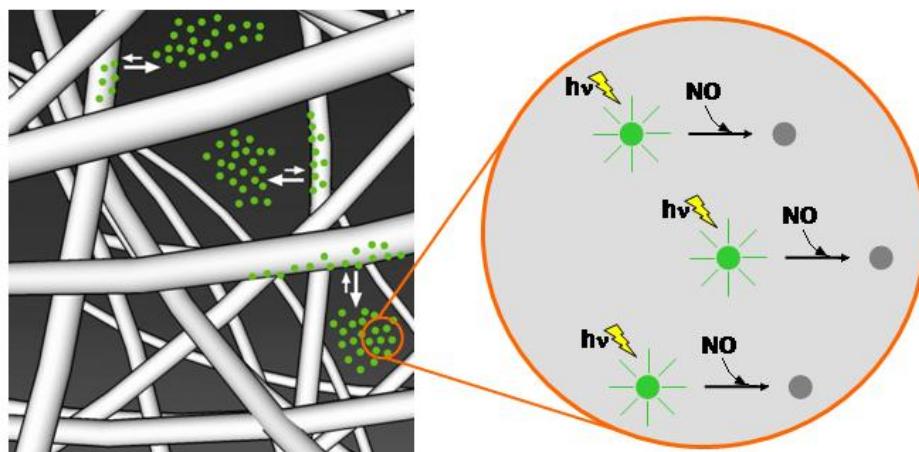


Figure 1. Proposed model for the entrapment of quantum dots (green dots) within the *solvent pools* of the studied organogel (left), and fluorescence quenching of QDs when interacting with gaseous nitric oxide (NO) (right).

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From the steady-state and time resolved fluorescence measurements here reported, the location of QDs inside the organogel matrix can be hypothesized at the *solvent pools* created by the self-assembly of organogelator, in close agreement with our previous findings in other studied organogel-probe composite materials [3,4].

Moreover the good analytical response to gaseous NO suggests that it would be possible to use the developed materials in nitric oxide sensor devices, specially taking into account that the semisolid state of the organogel is preserved after the interaction with NO. Hence, this type of new materials could be of interest for a number of analytical applications in Biomedicine or Environmental Science.

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PS-42 – Versatile Photoactive Materials Based on Zeolite L doped with Laser Dyes

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The incorporation of organic photoactive molecules into nanostructured solid host is an active area of research [1]. Such materials offer many advantages for the development of new versatile optoelectronic devices. The rigid environment of the solid host protects the organic molecule against chemical or photochemical attacks and increases its thermal resistance. Moreover, such constrained framework forces the guest to adopt a preferred orientation giving rise to a fully aligned system. In this sense, antenna devices consisting in a host characterized by a nanoscaled channels and doped with different fluorophores seem to be a promising research area. These systems try to imitate the natural photosynthesis process where solar radiation of different energy is collected and transported to the desired reaction center with the adequate energy via successive energy transfer processes.

Actually there is a wide variety of laser dyes susceptible to be allocated by their size in nanoporous materials and covering the ultraviolet and visible region. Present work deals about the incorporation of fluorophores emitting in different regions of the visible (DMPOPOP in the blue region, BODIPY in the green-yellow and Oxazine in the red) into zeolite L, an aluminosilicated with one-dimensional channels running along the crystal with a pore diameter of about 7.1 Å (Figure 1). Both commercial zeolite L (Lucidot) and ourselves synthesized zeolite L by a hydrothermal method assisted by microwave energy, have been employed.

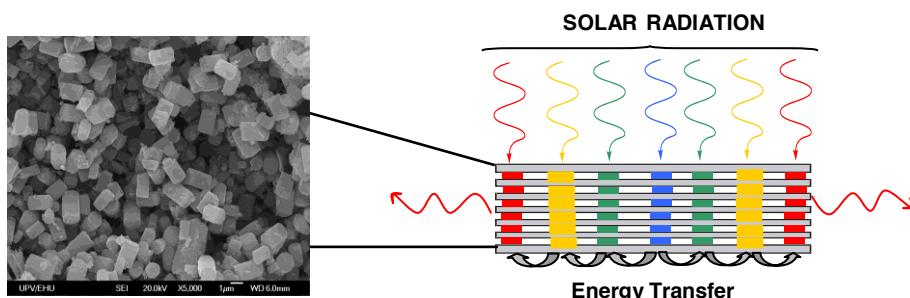


Figure 1. A) SEM image of zeolite L crystals synthesized by ourselves; B) Antenna system where the energy transfer takes place between different fluorophores.

The resulting dye-doped material is fully characterized by steady-state and time-resolved photophysical techniques. The pores of zeolite L are filled with a high amount of dyes, exclusively in monomeric form and aligned in a preferential orientation, thus, giving rise to an organized photoactive material. This ordered disposition of the dye in the zeolite L

nanochannels was confirmed by confocal fluorescence microscopy. The intramolecular energy transfer between the dyes takes place in the zeolite channels since the excitation of the donor molecules located in the centre of the crystals gives rise to the emission of the acceptors in the entrances of the pores (Figure 2). Such energy transfer processes in the solid state are the key factor in the development of new photonic devices. On one hand, this phenomenon is applied in antenna systems where light of different energies is harvested and transferred by successive efficient energy hops to the reaction centre and with the desired energy [2]. On the other hand, if such energy transfer is not so efficient, emission bands in the whole visible part (blue, green and red) can be achieved. The sum of these emissions results in a white light emitting devices [3].

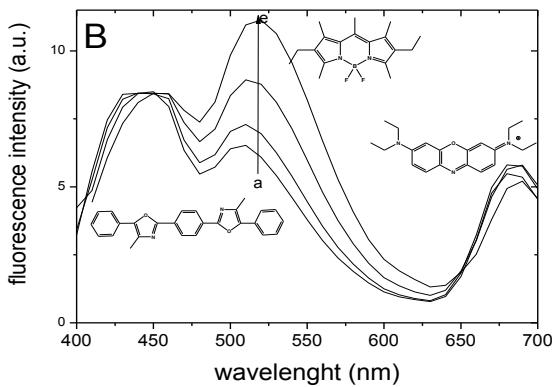


Figure 2. Normalized time-resolved emission spectra of DMPOPOP,PM567,Ox1 doped zeolite L, registered at different times after excitation at 370 nm: a-0.24 ns; b-1.22 ns; c-3.05 ns; d-3.72 ns; e-6.51 ns.

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PS-43 – Phototriggered drug release from a supramolecular assembly

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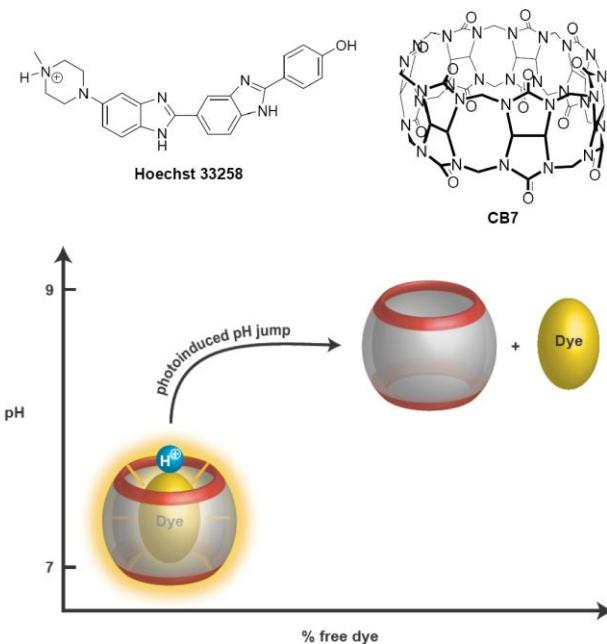
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The stimulation of supramolecular assemblies with light (“photoswitching”) may constitute an elegant approach for targeted drug delivery with macrocycles [1]. In particular, the use of light pulses for this purpose bears advantages like the possibility of spatiotemporal and remote control. In the simplest case, the photoisomerization of a drug guest may be used for this objective. However, this requires photoactivity, which is not fulfilled by all drugs. A conceptually alternative approach is the use of a photoinduced process that triggers a relay mechanism through which the drug can be released.



Scheme 1. Structures of Hoechst 33258, cucurbit[7]uril (CB7), and disassembly of the Hoechst 33258•CB7 complex by a photoinduced pH jump.

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In the present work we used a supramolecular host-guest complex formed between Hoechst 33258 as model DNA-intercalating drug [2] and cucurbit[7]uril (CB7), a recently intensively explored macrocyclic host [3-5]. It is well-established that the formation of complexes with CB7 shows pronounced pH dependence [4,5]. With general character, at low pH, guests are complexed with higher binding constants, while pH increase leads to weaker binding, resulting in decomplexation. Hence, a photoinduced pH jump may serve our objective to achieve a light-triggered decomplexation of Hoechst 33258 from its CB7 complex. Additionally, on the one hand this dye is fluorescent while encapsulated by CB7, and on the other hand, it is practically non-fluorescent as free molecule ($\Phi_f = 0.74$ *versus* 0.01). This enabled us to follow the event of disassembly of the host-guest complex by conveniently monitoring the fluorescence response of the system [6].

The photoinduced pH jump was achieved with the photobase malachite green leucohydroxide, which upon radiation with UV light produces the malachite green cation as well as hydroxide ions with high efficiency [7]. This compound led upon UV irradiation to a sudden increase in pH from 7 to 9, which was accompanied by a drop of the Hoechst 33258 binding affinity to CB7 by *ca.* 2 orders of magnitude ($K_b = 1.7 \times 10^6 \text{ M}^{-1}$ *versus* $2.8 \times 10^4 \text{ M}^{-1}$). In summary, the drug is effectively released (see Scheme 1).

The experimental details and photophysical/supramolecular characterization (UV/vis absorption and fluorescence spectroscopy, NMR spectroscopy, ESI-MS spectrometry) of the dye•CB7 complex will be discussed in detail.

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PS-44 – Photochemistry of Matrix Isolated Isoniazid

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Isoniazid (or isonicotinic acid hydrazide, INH; see Figure 1) has a high activity against *Mycobacterium tuberculosis* (the microorganism responsible for the tuberculosis disease) and is still the most widely used drug in antituberculous regimens [1,2].

In this study [3], the structure, spectroscopy, and photochemistry of INH were studied by low-temperature infrared spectroscopy and quantum chemistry calculations. According to DFT(B3LYP)/6-311++G(d,p) calculations, 12 minima were found on the potential energy surface of the molecule, corresponding to two *cis* conformers about the O=C-N-N axis (C1, C2) and one form *trans* about this axis (T), all being 4-fold degenerate by symmetry. The C1 conformer was predicted to be more stable than T and C2 by 20.4 and 22.6 kJ mol⁻¹, respectively.

After UV ($\lambda > 235$ nm) irradiation of the matrix-isolated isoniazid, the compound was found to undergo photolysis through two different pathways: a Norrish type I α -cleavage leading to production of isonicotinaldehyde and N₂H₂, and a concerted sigmatropic reaction with production of pyridine, CO and N₂H₂. The latter reaction was found to be nearly two times faster than the former in both argon and xenon matrixes. In addition, both reactions were found to be disfavored in a xenon matrix, which is in consonance with the involvement of (n, π^*) excited states in both photochemical processes.

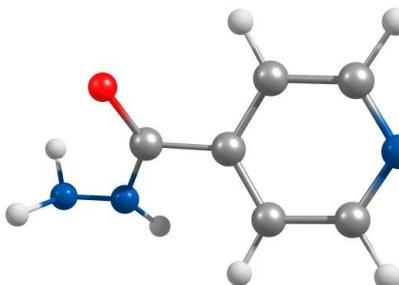


Figure 1. Molecule of INH.

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Acknowledgement. This work was supported by FCT (Projects PTDC/QUI/71203/2006 and PTDC/QUI-QUI/111879/2009), CYTED (108RT0362), and ANPCyT (Project PICT/2006/0068). A. B. acknowledges FCT for the award of a pos-doctoral Grant (SFRH/BPD/66154/2009). A.G.Z. is member of the Research Career of CONICET (National Research Council, Argentina).

PS-45 – Conformational and specific solvent effects on the photophysics of distyrylbenzene and distyrylstyrene oligomers in solution

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Conjugated organic polymers are playing a major role within the developing field of plastic electronics, due in particular to their applications in light-emitting diodes, thin film transistors, photovoltaic devices and sensors. Nowadays, a major topic of research is the understanding of their optical and electronic properties to the development of different polymer structures. One possible approach is the study of conjugated oligomers, which are simpler to synthesize, and are monodisperse. These are described by a small number of repeat units containing an electronically π -delocalized backbone. Here, a series of organic *para*-phenylenevinylene oligomers containing dialkylamino groups at the termini, were synthesized, and characterized (see Figure 1). The photophysical and solvatochromatic properties of oligomers, with three, four and five phenyl groups, were investigated through steady-state and time-resolved fluorescence.

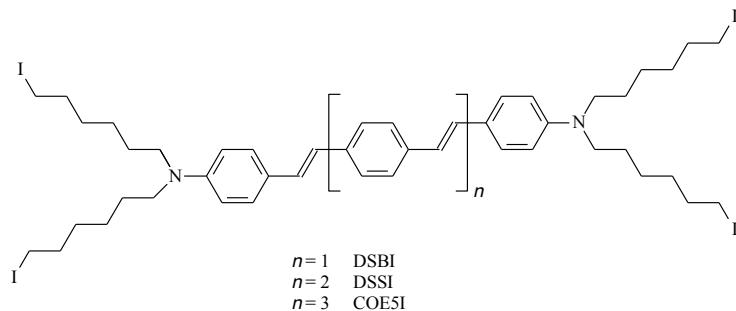


Figure 1. Chemical structure of the oligomers

The general photophysical behavior was studied of these oligomers in solvents of different polarity. The decrease of the solvent polarity leads to small shifts in different solvents, large blue-shifts of the emission spectra and increase in the fluorescence quantum yield. Comparison of the effect of chain length on the absorption and emission spectra shows that

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the increase of the oligomer length is consistent with an extension of the conjugation length, i.e., a red-shift is observed in the maximum absorption and emission wavelengths.

Global analysis of the fluorescence decays collected at different emission wavelengths, were found to be bi-exponential, in toluene. The longer time, appears as a decay component at all emission wavelengths and varies from 930 to 840 ps, with increasing chain length. The shorter time (8-25 ps) appears as a decay at the onset of the emission spectrum and as a risetime at longer wavelengths. In similar systems, this component has been previously interpreted in terms of fast conformational relaxation of the initially excited polymer/oligomer, into a more planar conjugation [1,2]. However, in our case this hypothesis was excluded by solvent and temperature dependence studies, i.e., the dependence of the fast component with solvent and temperature is not the expected for a dynamic process related with the viscosity of the solvent. Thus, this component is probably due to specific interaction between the oligomer main chain and the solvent. Molecular dynamics simulations, Møller-Plesset 2 and DFT calculations were performed to provide further details about the conformational processes of the oligomers in solution.

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Acknowledgement: Telma Costa acknowledges the Portuguese Science Foundation (FCT) for a post doc grant (Ref. SFRH/BPD/47181/2008). LLGJ aknowledges FCT for the post-doctoral grant SFRH/BPD/26415/2006 and the "Laboratório de Computação Avançada", of the Department of Physics of the University of Coimbra, for the computing facilities.

PS-46 – Photophysics of short poly(acrylic acid) chains labelled with pyrene

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The photophysics of poly(acrylic acid) (PAA) with high (450 000 and 150 000 kg/mol) and low molecular (2 kg/mol) weight randomly labelled with different degrees of pyrene (Py) has been previously investigated in different media and conditions [1-4]; in the present study we have selected the low M_w PAA polymers with five different loadings of pyrene, Figure 1, (acronym PAAMePy(2)12, 18, 24, 41 and 133) and investigated these in organic solvents and water by means of steady-state and time-resolved fluorescence techniques.

The dynamics of these polymers showed to display a complex photophysical behavior resulting from the coexistence, within a single polymer chain, of monomers that do not form excimers (M_A), monomers (M_B) that give rise to one excimer (E) or two excimers, E_1 and E_2 , (which can be either formed via dynamic or static mechanisms) [1,2]. In organic solvents the kinetic scheme is reduced to the M_A , M_B and E species (Fig. 2).

In the case of the investigated low M_w polymers, hydrophobically modified with Py, it was seen that more than 90% of the chains are not labelled or are single labelled, 1-5% double labelled and less than 1% has three or more tagged pyrenes. Excimer formation is thus essentially a consequence of the dynamics of the double labelled polymer chains. Molecular simulation studies of "labelled" PAA were also performed aiming to further understand the contribution of the labelling degree and position of the hydrophobic probe in the PAA skeleton to the observed behavior. The overall data were interpreted on the light of the distinct kinetics schemes (found for different media) which seem to indicate that excimer formation is, in these polymers, mainly due to interactions pyrene-pyrene located at short distances

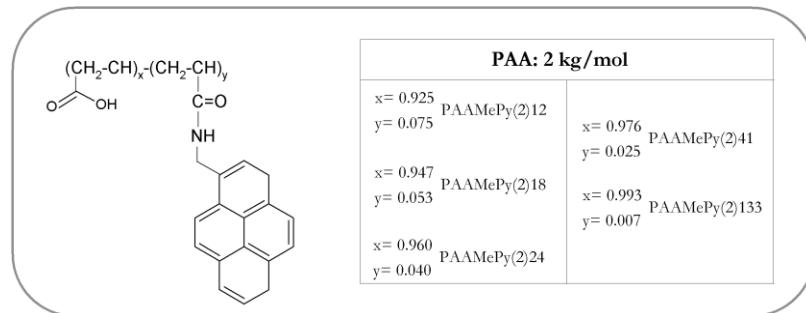


Figure 1. Relative compositions (PAA vs. Py units) of some used polymers and their acronyms.

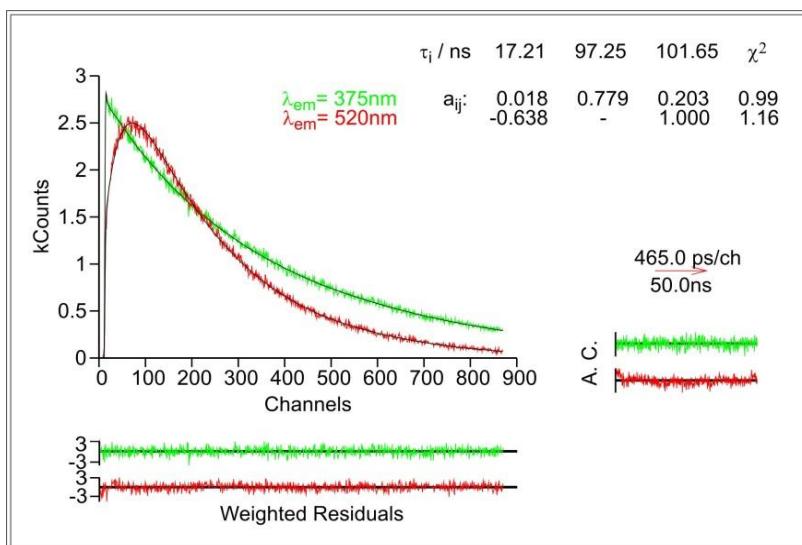


Figure 2. Fluorescence decay collected at the monomer ($\lambda_{\text{em}} = 375$ nm) and excimer ($\lambda_{\text{em}} = 520$ nm) emission wavelengths for PAAMePy(2)24 in dioxane (at room temperature and $\lambda_{\text{exc}} = 339$ nm).

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PS-47 – BODIPY compounds bearing nitro and amino groups. From highly efficient fluorophores to fluorescent sensors.

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Nowadays Boron DiPyrromethene fluorophores (herein BODIPY) is probably one of the most widely known laser dye families with application in many and diverse technological fields [1]. They are not only used in lasers but also in antenna devices solar cells and in biomedicine as photodynamic therapy agents or sensors, among the most important applications. This is due to their unique photophysical properties which can be modulated by means of the substitution pattern. In fact, BODIPY dyes usually present strong absorption, fluorescence and lasing bands in the middle part of the visible. However, the incorporation of appropriate functional group onto the chromophore could lead to new photophysical processes or large spectral shifts. Thus, the type of substituents and the position in which they are attached to the chromophore allows obtaining, for example, a highly fluorescence dye in the red part of the visible or a system which fluorescence properties are sensitive to a certain property of the surrounding environment.

Therefore, one should choose carefully the kind of substituents and the position in which they will be incorporated to BODIPY depending on the desired application. Recently, a straightforward synthetic methodology has been developed to add nitro groups selectively and specifically to the desired position of the BODIPY chromophore. The subsequent reduction of the nitro group leads to the corresponding amino derivatives. Afterwards, this amino group could act as precursor for the incorporation of a wide variety of substituents. These amino and nitro groups are adequate leaving groups to incorporate different substituents, opening the way to a huge variety of BODIPY derivatives.

Present work is focused on the photophysical characterization and quantum mechanical simulation of amino and nitro derivatives of an asymmetric alkyl BODIPY (Figure 1). The addition of an amino group at 5 position induces a bathochromic shift of the spectral bands while maintaining the high fluorescence ability characteristic of BODIPY dyes. The key role of the chromophoric position of the substituent is pointed out by a previous work where the attachment of the same amino group but in the central position induced a contrary and strong blue shift of the spectral bands [2].

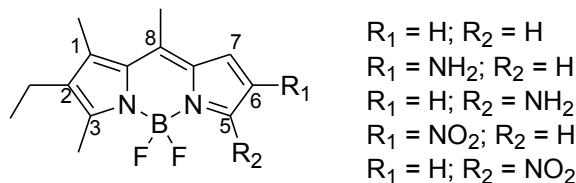


Figure 1. Nitro and amino derivatives of BODIPY.

On the other hand, the presence of the nitro groups has a deleterious effect in the fluorescence emission (mainly in the BODIPY derivative bearing the nitro group at the 5 position). Furthermore, the fluorescence ability is drastically quenched in polar solvents. The nitro group is characterized by its high electron withdrawing nature as it is pointed out in the theoretically calculated electrostatic potential maps or electronic charge distribution (Figure 2). Such electron removal effect induces the presence of a non-fluorescence intramolecular charge transfer state (ICT) which quenches the fluorescence emission especially in polar media. Therefore, these nitro BODIPY are not suitable as laser dye but yes as polarity sensors since the polarity of the surrounding environment of the dye can be followed from the fluorescence ability evolution.

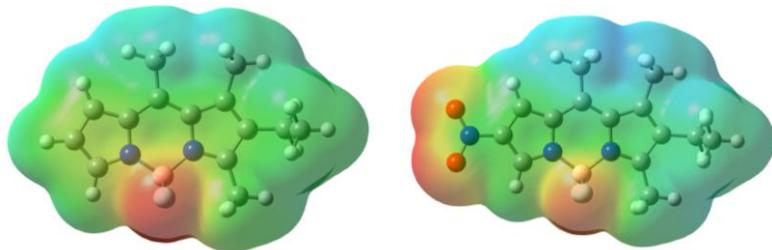


Figure 2. Electrostatic potential mapped onto the electronic density for the reference alkyl BODIPY and its 6-nitro derivative (red-negative and blue-positive).

[1] a) A. Loudet, and K. Burgess, *Chem. Rev.*, **107**, 4891-4932 (2007); b) G. Ulrich, R. Ziessel, and A. Harriman, *Angew. Chem. Int. Ed.*, **47**, 1184-1201 (2008); c) M. Benstead, G. H. Mehl, and R. W. Boyle, *Tetrahedron*, **67**, 3573-3601 (2011).

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PS-48 – BODIPY-anthracene pseudopeptidic fluorescent dyads

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Pseudopeptidic compounds have attracted the interest of many researchers in several areas. They have properties of great interest as they concentrate in a small space a large number of functional groups capable of participating in supramolecular interactions with other species. Interesting biomedical activities have been detected in some synthetic peptidomimetics due to the peptidic fraction, which usually makes them highly biocompatible and at the same time allows further molecular diversity [1].

Fluorescent compounds have gained great importance in recent years due to the high relevance they have in the field of bioanalysis, acting as sensors of several species of interest such as protons, Zn^{II}, Mg^{II}, Cu^{II}, Cu^I, chloride, nitric oxide, singlet oxygen and hydroxyl radicals, among others [2]. They are essential tools, since they offer high analytical sensitivity and real-time detection capabilities [3].

Since pseudopeptidic compounds are used, for example, in the development of new receptors in different fields of Molecular Recognition and Supramolecular Chemistry, fluorescent compounds based on pseudopeptidic structures might be useful as fluorescent sensors of biological species. Taking it into account, in our research group several fluorescent peptidomimetics have been developed in recent dates, being sensitive to pH, with applications in cellular studies [4], as well as various fluorescent supramolecular receptors for amino acids [5].

On the basis of this background, the synthesis of new peptidomimetic compounds analogous to those described above, but with double excitation/emission was proposed. In this work a novel family of pseudopeptidic bichromophoric multifunctional compounds showing dual excitation capabilities has been synthesized using a combination of two fluorescent units in their structure.

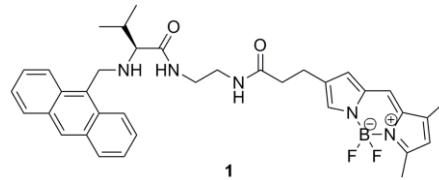


Figure 1. BODIPY-anthracene dyad (**1**) belonging to the new family of pseudopeptidic bichromophoric multifunctional compounds.

Initial experiments were carried out using anthracene as a common chromophore, together with pyrene, dansyl and NBD. Best results, however, have been obtained with compound **1** containing BODIPY (borondipyrromethene) as the second fluorophore. This new bichromophoric compound has been characterized by means of ¹H-NMR, ¹³C-NMR, IR, Raman, ESI-MS.

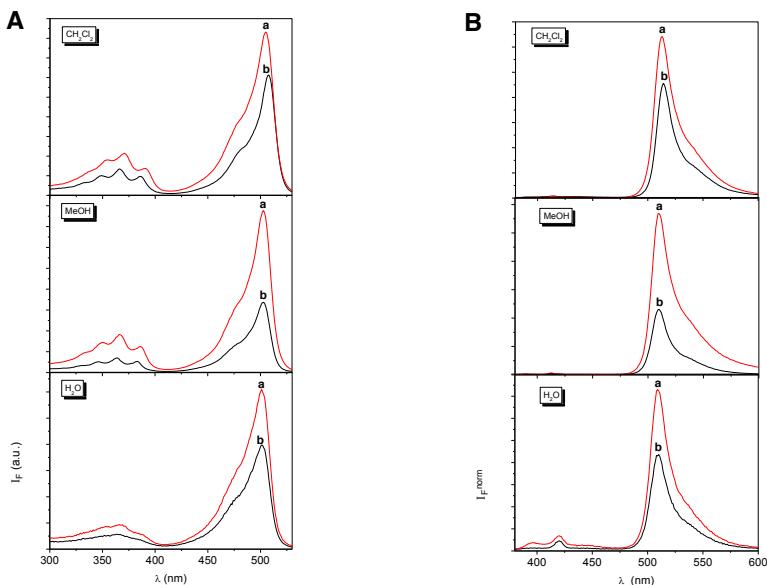


Figure 2. **A)** Excitation spectra (em. 550 nm) and **B)** emission spectra (exc. 367 nm) in both (a) acidic and (b) neutral medium using different solvents.

Fluorescence studies in several media have been performed in order to characterize the compounds from the photophysical point of view. Figure 1 shows the excitation and emission spectra of compound **1** in several experimental conditions. As it can be seen, the excitation spectra of **1** is composed of two bands corresponding to BODIPY and anthracene chromophores, whereas the emission spectra (exciting at 367 nm) in all the cases show only the fluorescence of the BODIPY fluorophore, which points out to an intramolecular energy transfer process.

The studies carried out so far also reveal the potential future use of the synthesized compounds as supramolecular sensors.

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PS-49 – Synthesis and Laser Behavior of New Nitro and Amino BODIPYs

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4,4-Difluoro-4-bora-3a,4a-diaza-s-indacenes, commonly known with the trademarked name BODIPY, are a class of fluorescent dyes that are finding an increasing number of applications in both the materials and optical imaging fields. The interest in BODIPYs originates from their outstanding photophysical properties, such as high absorption coefficient, high fluorescence quantum yield, high photostability, and low sensitivity to medium effects [1]. A wide variety of reactions can be carried out in the BODIPY to produce a shift in the absorption and emission wavelengths.

BODIPY dyes are intrinsically electron rich and they will react with electrophiles. Recently, our research group has carried out a study on the reactions of iodination and fluorination in BODIPYs with different degree of substitution [2].

Continuing the study, we were interested in the nitration reactions. As we know, exists in the literature an example of nitration in the BODIPY core in 2- and 6-positions [3]. In addition, there are several Japanese patents with two dinitro derivatives but not described their synthetic methods or their spectroscopic data [4]. However, there are numerous examples of BODIPYs with nitro groups but not directly attached to the BODIPY core and most of them are used as precursors of amino groups [5].

We have synthesized a series of new nitro derivatives. In addition, the nitro BODIPYs obtained are easily transformed into the corresponding amino derivatives (Figure 1), that are precursors of ammonium groups or can be act as nucleophiles against halogenated BODIPY derivatives.

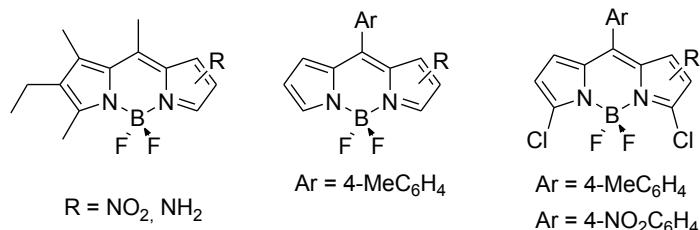


Figure 1

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The position in which nitro and amino groups are attached in the BODIPY core, modulates their laser properties.

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PS-50 – Development of excellent long-wavelength BODIPY laser dyes with a strategy that combines extending π -conjugation and tuning ICT effect

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In the biophotonics related fields, laser dyes with long wavelength emission (>600 nm) offer clear advantages because long wavelength light can penetrate deeper into tissues [1], increasingly their applications in surgical treatment and photodynamic therapy (PDT). In addition, for *in vivo* imaging, the long wavelength probe's fluorescence does not interfere with biological background fluorescence which is in shorter wavelength region [2]. Although dyes with red-edge emission are in great demand, there are only a few with satisfactory properties suitable for extensive applications. Most usual dyes exhibit drawbacks such as relatively low fluorescence quantum yields, poor photostability, difficulty in synthesis and derivatization, and/or poor biological compatibility.

By comparison and combination of two strategies, extending π -conjugation [3] and tuning Intermolecular Charge Transfer (ICT) [4] effect, new long-wavelength BODIPY dyes have been efficiently synthesized.

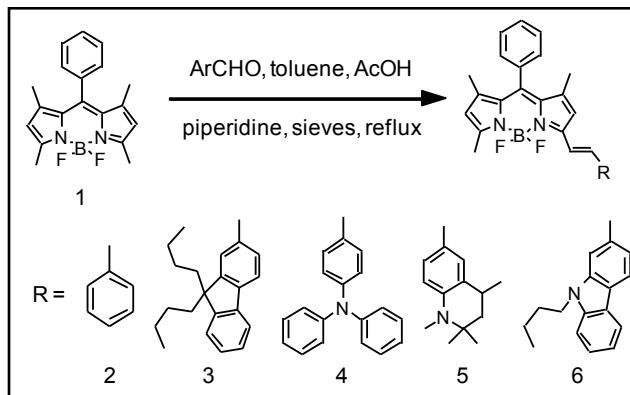


Figure 1. Synthetic route to obtain BODIPY derivatives **2-6**.

The new chromophores exhibit good optical properties: high fluorescence quantum yields, exceptionally large molar extinction coefficients, narrow red-emission bands, and relatively large Stokes shifts, in polar and apolar solvents. Besides, the new dyes, under transversal pumping at 532 nm, exhibit high efficient (up to 57%) and stable laser emission (after 75 000

pump pulses, compounds **2**, **3** and **6** maintain their initial laser energy without sign of degradation) tunable from green to NIR spectral region (560-740 nm).

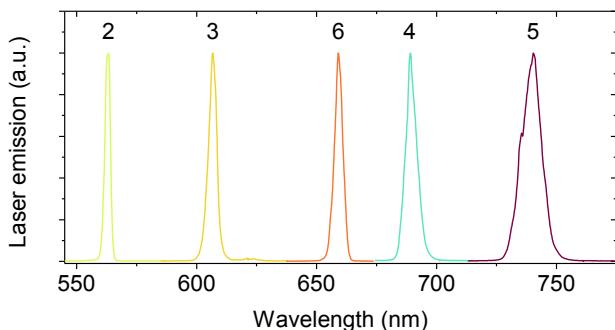


Figure 2. Laser emission in the green-red spectral region from the new dyes pumped at wavelengths near their absorption maxima.

Moreover, compound **6** shows cell membrane permeability and bright intracellular red fluorescence, while the cells remain viable and no apparent toxicity and side effects have been observed throughout the imaging experiments.

These advantageous characteristics assure the potential of these dyes for biophotonic applications.

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PS-51 – The Supercontinuum Laser as a Flexible Source for Quasi-Steady State and Time Resolved Fluorescence Studies

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Commercial Fluorescence Lifetime Spectrometers have long suffered from the lack of a simple, compact and relatively inexpensive broad spectral band light source that can be flexibly employed for both quasi-steady state and time resolved measurements (using both Time Correlated Single Photon Counting (TCSPC) and Multi-Channel Scaling (MCS) techniques).

This paper reports the integration of an optically pumped, photonic crystal fiber, supercontinuum source [1] with a pulse picker (Fianium model SC400PP) as a light source in a combined Steady State and Fluorescence Lifetime Spectrometer (Edinburgh Instruments model FLS920), with double excitation and emission monochromators and with single photon counting detectors (micro-channel plate photomultiplier and a near-infra-red photomultiplier) covering the UV to NIR range.

The spectrally corrected output from the supercontinuum laser (repetition rate selectable up to 20MHz) has been measured over the range 375-1700nm and shown to have the same order of higher spectral brightness as a 450W Xenon lamp over the majority of the range. The pulse height distribution and leading edge jitter of the output pulses has been measured and the performance optimised.

Alternative methods to select the emission wavelength and bandwidth from the supercontinuum output will be reported. These include using a tunable acousto-optic filter with up to 16 channels, which can be superimposed to provide a variable bandwidth, or the novel use of two motorised linear variable wedge interference filters, one low pass and the other high pass. Performance will be contrasted and compared.

Although the master oscillator within the supercontinuum laser has a short pulse width of ca 6ps it is known that the output pulse is significantly broadened by dispersion in the optical fibre. A key parameter which controls the precision of a TCSPC measurement is the Instrumental Response Function (IRF), which has been measured and shown to be <150ps over the majority of the tuning range.

The “Proof of Concept” of using the supercontinuum laser as a source for TCSPC measurements has been shown by measuring several known materials. A sample of anthracene in cyclohexane (5×10^{-5} M) was studied as this is one of the most documented standards of fluorescence lifetime spectroscopy with a lifetime of 5.1ns when degassed. However, the excitation spectrum has a longest wavelength peak at 375nm with no absorption above ca 390nm. This showed the supercontinuum laser can be used at these short wavelengths. More challenging applications to measure shorter lifetimes of erythrosine B in water (lifetime ca 88ps) and pinacyanol chloride (lifetime ca 13ps) with excellent “Goodness of Fit” parameter will be shown.

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By varying the repetition rate with the pulse picker, the supercontinuum laser is capable of measuring fluorescence lifetimes up to 50 μ s using the TCSPC. The possibility of using bursts of pulses in a variable envelope as a longer pulse width source for phosphorescence lifetime measurements in the micro- and milli-second range using the MCS technique will be discussed.

In conclusion, the supercontinuum laser offers the possibility of measuring fluorescence lifetimes down to a few 10's of picoseconds with the advantages of broadband tunability. The use of new supercontinuum sources with output further into the UV spectral region will be discussed.

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PS-52 – A molecular logic memory device

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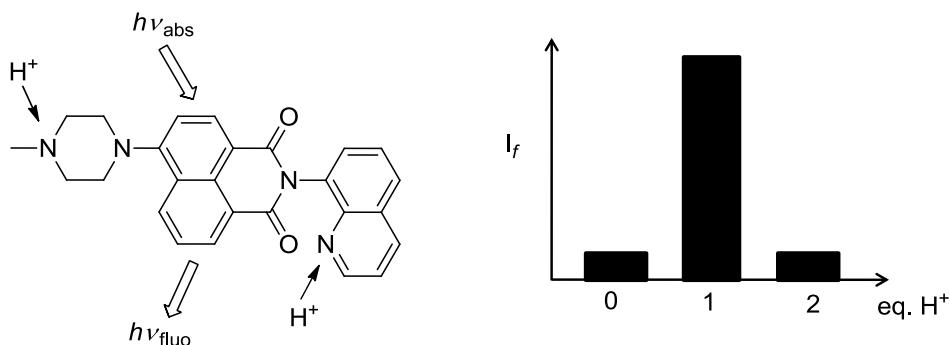
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The processing of binary information at the molecular level has received wide attention in recent years [1]. This is mainly based on the potential application of molecular logic devices in molecular computing [2-4.] However, more immediate applications of this conceptual approach in analytical chemistry, clinical diagnosis, pro-drug activation, and the design of smart materials have emerged recently. One important feature, which in this framework should be “taught” to molecules, is the quality of having a memory [5].



Scheme 1. A molecular OFF-ON-OFF switch.

In the present work we have chosen a new fluorescent triad comprising of a 4-amino-substituted naphthalimide derivative as fluorophore, a quinoline unit at the imide side and an electron-donating *N*-methylpiperazine unit in the aromatic 4-position. The latter two are both working as potential acceptors for proton inputs (Scheme 1). In the absence of input application the system has a low fluorescence due to excited state quenching by photoinduced electron transfer (PET). However, the addition of one equivalent of protons leads to fluorescence enhancement, due to the blocking of PET from the piperazinyl unit. Further addition of a second equivalent of acid leads again to a pronounced drop in emission,

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which is reasoned by the protonation of the quinoline unit. In brief, an *OFF-ON-OFF* fluorescent switch results [6]. Additionally, the molecule “remembers” its current state (no protonation or monoprotonation) and gives a differentiated fluorescence output upon addition of another equivalent of protons. Hence, the molecule has a memory. In the concrete, the binary behaviour of the molecular system is compatible with that of a T-latch.

The synthesis, photophysical characterization, and implementation of the logic memory function will be discussed in detail.

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PS-53 – Stress Degradation Studies on Pravastatin and Development of a Validated Stability HPLC Assay

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Pravastatin sodium, a mono-sodium salt of 1S-(1 α (β S, δ S,2 α ,6 α ,8 β (R),8a(α))-1,2,6,7,8,8a-hexahydro, β , δ , 6-trihydroxy-2-methyl-8-(2-methyl-1-oxobutoxy)-1-naphthaleneheptanoic acid, is an anti-hypercholesterolemic agent having an inhibitory activity against 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase, the rate-limiting enzyme in the cholesterol biosynthetic pathway. Although the HMG-CoA reductase inhibitors, statins, are structurally related, only Pravastatin is characterized as one of the best statins, due to the hydroxyl substituent attached to its decalin ring, which result in a greater hydrophilicity than other statins.

In this work, a simple and rapid stability-indicating high-performance liquid chromatographic (HPLC) method was developed and applied to study the hydrolytic behavior of Pravastatin which is highly hydrophilic compared with other statins like lovastatin, mevastatin or simvastatin. Pravastatin is clinically used as the active hydroxy acid, while the other three compounds are administered as prodrug lactones which, over a period of time, convert *in vivo* to their respective active hydroxy acid forms. For the hydrophilic inhibitor Pravastatin, chromatographic separation [1] was carried out isocratically using a C-18 column, 40 °C column temperature, acetonitrile-phosphate buffer 30 mM, pH 2.0 (28:72, v/v) as mobile phase at a flow rate of 1.0 mL with UV detection at 239 nm using a photodiode array detector.

The developed method exhibited an adequate repeatability, reproducibility and a good linear response. Also we performed forced degradation studies (chemical and physical stress testing) of Pravastatin which is essential to help to develop and to demonstrate the specificity of such stability-indicating methods. Stress conditions to which they were subjected were [2]: acid, basic and neutral hydrolysis adding HCl, NaOH and H₂O respectively; chemical oxidation with a treatment with H₂O₂ 30% (v/v); photochemical degradation was studied by exposing the stock solution to UV light (λ = 366 nm) for 10 hours; and finally thermal stress where bulk drug was subjected to dry heat at 105 °C for 5 hours. In each case was also measured its UV absorption spectrum which indicates whether the degradation process affect the chromophore structure of the drug under study. The method can be used for structure elucidation of degradation products and to determine the intrinsic stability of statin in solution and solid state as well as to reveal the thermolytic, hydrolytic, oxidative and photolytic degradation mechanism of Pravastatin.

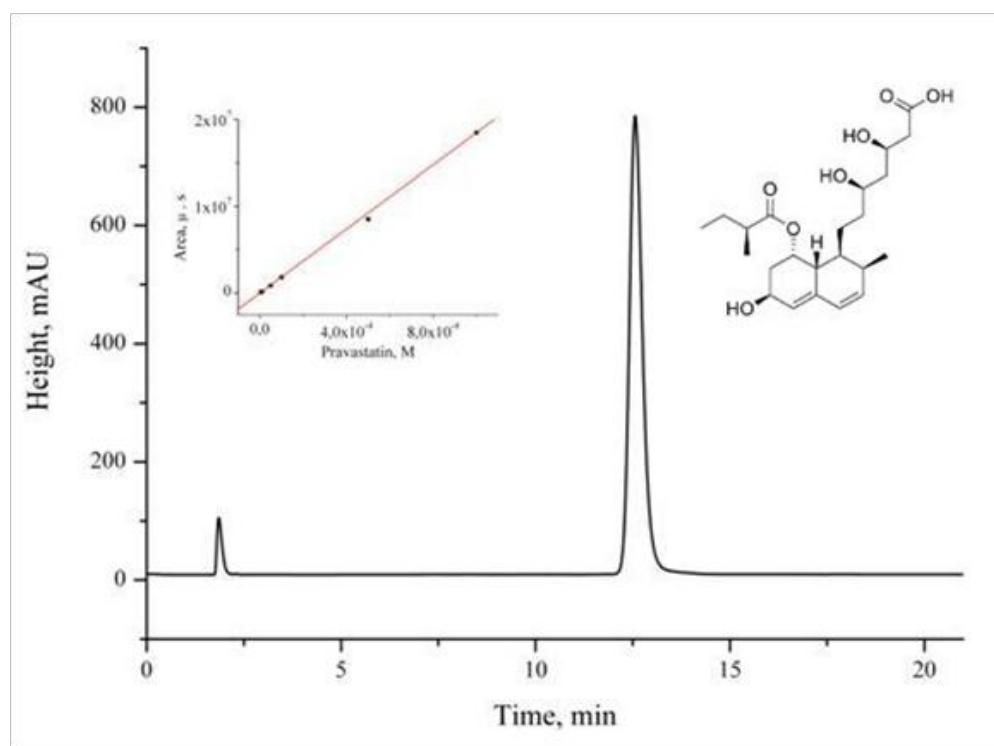


Figure 1. Chromatogram of a 1×10^{-3} M Pravastatin standard solution in the optimal experimental conditions selected with UV detection at 239 nm. It shows a retention time of 12.567 min. Inset: Calibration curve of Pravastatin [1×10^{-3} – 5×10^{-6} M] on each point is represented by its corresponding standard deviation, $AUC = -16204.0113 + 1.8505 \times 10^{10} [\text{Pravastatin, M}]$, $n=6$.

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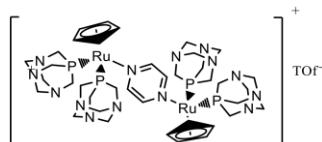
PS-54 – Visible light activity of the new water Soluble Ruthenium bimetallic Complex $[(\text{PTA})_2\text{CpRu}-\text{pyz}-\text{RuCp}(\text{PTA})_2]$ (PTA = fosaadamatane phoshine; pyz = pyrazine)

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Complexes containing the ligand PTA were used to obtain a new family of air-stable water-soluble poly-hetero-metallic polymers display lineal (1D) structure including PTA as a metal coordinating spacers between the bimetallic $\{\text{CpRu}-\text{CN}-\text{CpRu}\}^+$ and $\{\text{Au}(\text{CN})_4\}^-$ moieties.[1] The building blocks for this kind of new poly-metalloc-polymers are bimetallic ruthenium complexes in which metals are linked by a ligand. Bimetallic complexes with metals communicated electronically are interesting compounds with possible applications to microelectronic industry, nanotechnology and nanoscience, medicine, solar sensible devices, novel optical devices and sensors, etc.[2] But the interesting properties of the bimetallic complexes few of them are water soluble. Herein we report the synthesis of the new water soluble ruthenium complexe $[(\text{PTA})_2\text{CpRu}-\text{pyz}-\text{RuCp}(\text{PTA})_2]^+$ (Scheme 1) that display interesting optical (Figure 1) properties in water solution and solid state, as well as it is photoactive under visible light.



Scheme 1. $[(\text{PTA})_2\text{CpRu}-\text{pyz}-\text{RuCp}(\text{PTA})_2][\text{CF}_3\text{SO}_3]$

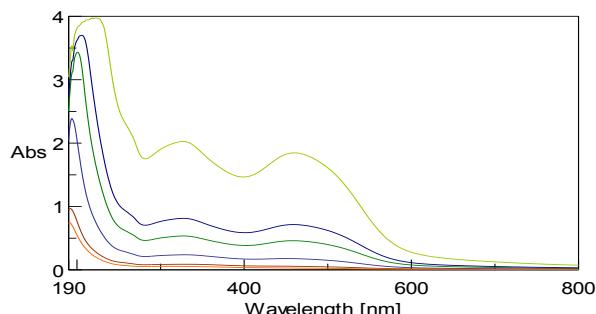


Figure 1. UV-Vis absorption spectra of $[(\text{PTA})_2\text{CpRu}-\text{pyz}-\text{RuCp}(\text{PTA})_2][\text{CF}_3\text{SO}_3]$ in water (concentration from 5×10^{-6} to 2.5×10^{-4} M). $\lambda_{\text{max}}/\text{nm}(\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1})$: 219 (18325), 327 (8078), 462 (7281).

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PS-55 – Fluorescence study on the imipenem hydrolysis by metallo-beta-lactamases BcI and BcII and inhibition induced by mesna and mesna + dimesna mixture

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Beta-lactamases (BLs) are classified into two broad groups: 1) serine beta lactamases (classes A, C and D) and metallo-beta-lactamases (MBLs, class B) which bind one or two zinc ions at their active site. The spread of MBLs is considered one of the major concerns in public health [1]. Carbapenemase activity and resistance to clinical serine beta-lactamase inhibitors are the main features of these enzymes which recently have been found disseminated in *Enterobacteriaceae* [2].

The presence of one or two Zn ions in MBLs affects their selectivity and efficiency hydrolyzing carbapenems. Such a circumstance makes very difficult to develop a broad-spectrum inhibitor for MBLs. Nevertheless, numerous attempts have been made to solve this problem specially using thiol-derivatives [3].

In a previous work we have dealt with the inhibition of commercial beta-lactamases BcI (serine beta-lactamase) and BcII (MBL) from *B. cereus*. Now we present the results obtained in the kinetic study of a) the hydrolysis of imipenem in the presence of BcI and BcII; b) the inhibition of this process by mesna (sodium 2-sulfanylethanesulfonate) and a mixture of mesna and its dimer dimesna (disodium-bis-2-dithioethanesulfonate).

Taking advantage of the natural fluorescence of BcI and BcII a complementary kinetic study has been carried out. The kinetic curves in the absence of inhibitors (fig 1A) show a characteristic fluorescence quenching which can be considered as a result of the formation of substrate-BcI binding as proved by the K_M values calculated from the experimental data. Besides, the increasing fluorescence occurring after the quenching, is considered as a result of the hydrolysis of BcII and the subsequent increasing in the amount of free enzyme. This explanation is according to the slower fluorescence increasing observed in the presence of mesna or mesna + dimesna mixture (fig 1B and fig 1C).

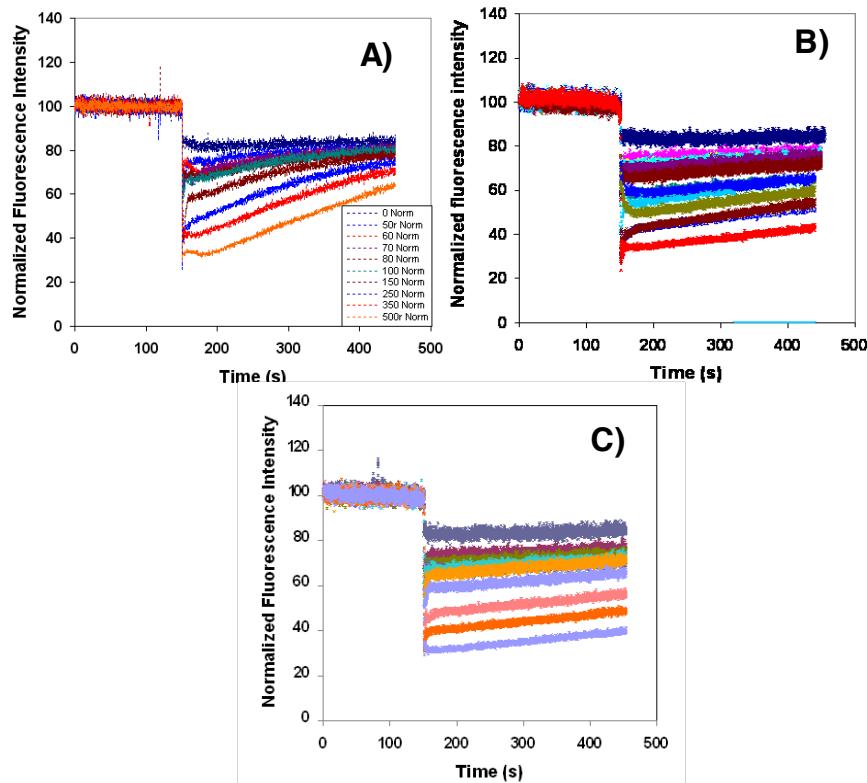


Figure 1. **A)** Normalized kinetic curves obtained from the fluorescence ($\lambda_{\text{exc}} = 280$ nm, $\lambda_{\text{em}} = 340$ nm) of a commercial sample of BcI + BcII from *B. Cereus* in the absence (upper curve) and the presence of increasing amounts of imipenem (Insert, 50r Norm: $0.397 \cdot 10^{-4}$ M-500r Norm: $3.97 \cdot 10^{-4}$ M) in a buffered medium MOPS pH 7.04 t°: 30 °C. The imipenem addition was made at 150 s; **B)** Normalized kinetic curves obtained in the same experimental conditions but in the presence of mesna ($5 \cdot 10^{-4}$ M); **D)** Normalized kinetic curves obtained in the same experimental conditions but in the presence of a mixture mesna + dimesna (estimated concentration $5 \cdot 10^{-4}$ M)

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Acknowledgement. B. Q. wishes to dedicate this work to the memory of his old fellows R. Sastre and R. Suau. This work was supported by University of Granada translational grant to E.M.P.

PS-56 – Degradation and detoxification of banana postharvest treatment water using advanced oxidation techniques

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The elimination and detoxification of water contaminated with the principal commercial fungicide - imazalil sulphate (Fruitgard IS 7.5) - used in the postharvest treatment of many fruits, including bananas [1] was successfully achieved through the use of advanced oxidation processes (AOPs). The techniques tested were heterogeneous photocatalysis with TiO₂ and Fenton processes. The evolution of fungicide concentration during degradation was studied together with mineralization and toxicity levels [2].

Among the photocatalytic techniques studied several catalysts were used, including the commercial Degussa-P25, and several catalysts synthesized or modified in our laboratory, such as Degussa P25 doped with Pt, and a new catalyst calcined at 1023K [3].

The initial concentration of imazalil sulphate in this study was 50 mg·L⁻¹. When considering the fungicide degradation, results were similar at different pH conditions rehearsed (3, 5 and 7), for both the commercial Degussa-P25 and the home-made catalyst named ECT1023t. However, TOC results better efficiency at pH 5 for Degussa-P25. Specifically, TOC removal was 55.9% at pH 3, 68.5% at pH 7 and 80.4% at pH 5.

The degradation of imazalil sulphate through the different treatments returns removal efficiencies between 99.2 and 99.9%, as shown in Figure 1.

For the photocatalytic TiO₂ systems at pH 5, the platinized catalyst t is the least efficient, while the home-made catalyst (ECT1023t) achieved the highest fungicide removal during the first 60 minutes of reaction. The removal of imazalil sulphate after 60 minutes, using the synthesized catalyst, was between 99.5 and 99.7% whatever the pH conditions (3, 5 or 7). However, Degussa-P25 showed a removal efficiency of 99% at pH 5 and 7, but 97% at pH 3. At low remaining concentrations of imazalil sulphate (after long reacting time), the efficiency of Degussa-P25 and ECT1023t catalysts become similar, obtaining in both cases the reduction of imazalil sulphate concentrations below 0.1 mg·L⁻¹.

The Fenton process was optimized by the determination of the appropriate concentration of reactants (Fe²⁺/H₂O₂). In Figure 1 has been included a Fenton reaction with 0.025 mg·L⁻¹ Fe(II) and 12 mM H₂O₂. We can observe that this technique returns the highest removal efficiency, obtaining a 92.6% removal of imazalil sulphate in the first minute of the process.

However, even though the Fenton process is simpler in terms of system design, further studies on a prototype or industrial scale system should be investigated, the use of H₂O₂ must be controlled if the objective is to reuse the treated water for irrigation, due to the toxicity of this reactant.

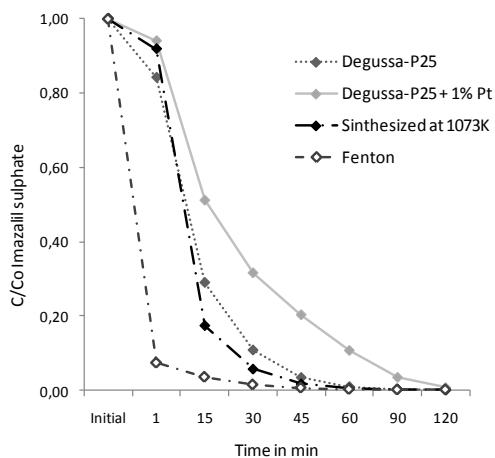


Figure 1. Imazalil sulphate degradation during the treatment with different oxidation techniques of a 50 mg·L⁻¹ aqueous solution.

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PS-57 – Photophysics of the interaction between a fluorescent xanthene dye and Ficoll

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The xanthene dye 9-[1-(2-Methyl-4-methoxyphenyl)]-6-hydroxy-3H-xanthen-3-one (TG-II) is highly sensitive to phosphate concentrations.^{1,2} Specifically, the autocorrelation function and the fluorescence lifetime can be considered direct and sensitive means of investigating the environmental phosphate concentration in small volumes at near-physiological pH.

As TG-II is potentially useful for probing intracellular phosphate-ion concentrations, we report the behaviour of the dye in a medium that mimic the intracellular environment. This environment is highly crowded due to the presence of large amounts of soluble and insoluble biomolecules. For mimic the crowded cell environment, we use Ficoll; a sucrose polymer widely used as a crowding agent because it is believed to be non-interacting and is composed of mixed sizes such that smaller and larger diffusing solutes can be studied.

However, in this work, we show that Ficoll is not an inert crowding agent in the presence of xanthene dyes such as TG-II. We report on the behaviour of the TG-II–Ficoll system, describing the spectral characteristics of this system in aqueous solution by means of absorption spectroscopy, steady-state fluorescence, time-resolved fluorescence, species-associated spectra (SAS) and fluorescence lifetime correlation spectroscopy (FLCS)

In resume, the most important new TG-II spectral characteristics in the presence of Ficoll are the next:

- Isosbestic point in absorption spectra with addition of Ficoll at high pH (Figure 1a)
- Fluorescence intensity increases at low Ficoll concentration and decreases at high Ficoll concentration (Figure 1b).
- Increasing of TG-II lifetime from 3.72 to 4.12 ns and appearance of a new lifetime of 1.91 ns

With this information we find two different behaviours in TG-II:

- The increment in the lifetime of TG-II (3.72→4.12 ns) and the increase in the fluorescence intensity when Ficoll concentration is low (Figure 1b) indicate that Ficoll produces a protection from solvent quenching increasing the emission fluorescence of the dye.
- The isosbestic point visualised in the absorption spectra (Figure 1a), the different steady-state fluorescence spectra observed when the Ficoll concentration is sufficiently high (Figure 1b), and the new lifetime of 1.91 ns recovered from solutions in the presence of Ficoll indicate the formation of a new species between TG-II and Ficoll in aqueous solution. Using SAS we have characterized the emission spectrum of the complex (Figure 2).

Finally, to confirm the interaction between TG-II and Ficoll we have used FLCS to obtain the diffusion coefficient of:

Free TG-II	$330 \mu\text{m}^2/\text{s}$
Free TG-II in Ficoll	$174 \mu\text{m}^2/\text{s}$
Complex TG-II-Ficoll	$20.1 \mu\text{m}^2/\text{s}$
Ficoll ³	$23 \mu\text{m}^2/\text{s}$

These results are consistent with the formation of an adsorption complex. Therefore, our overall data clearly demonstrate that Ficoll is not an inert crowding agent when in the presence of xanthene dyes.

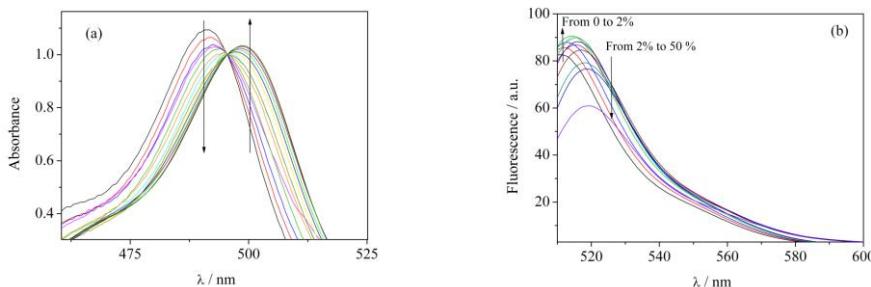


Figure 1. Absorption (a) and emission (b) properties of TG-II ($4 \times 10^{-6} \text{ M}$) in crowded aqueous solution at pH=9.5 in the presence of Ficoll concentrations between 0 and 50 %.

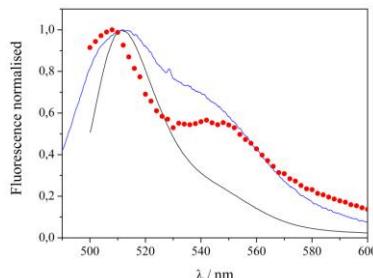


Figure 2. Normalised spectrum from the 1.91-ns component lifetime (●) and emission spectra recorded for both neutral (broken line) and free aqueous anion TG-II (solid lines)

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PS-59 – Metal enhanced fluorescence of sulfonated aluminium phthalocyanines induced by gold nanoparticles in layer-by-layer assembled systems

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The optical properties of fluorophores nearby metallic nanoparticles or nanostructured metallic surfaces are greatly affected by the interaction with metal free electrons (plasmons). The electromagnetic field induces an increase in the fluorophore radiative decay rate which is reflected by an increase of fluorescence intensity and a decrease of fluorescence lifetime. This phenomenon is known as Metal Enhanced Fluorescence (MEF) [1-3].

In this communication we present some evidences of MEF observed in systems containing aluminium sulfonated phthalocyanines (AlPcS_4 and AlPcS_1) and gold nanoparticles (AuNPs).

The following schemes were applied to two phthalocyanines separated at controlled distances from metal nanoparticles using the layer-by-layer assembly of polyelectrolytes: a) hollow microcapsules loaded with AuNPs; b) nanocapsules templated on the AuNPs (Figure 1); and c) 2D multilayered films supported on glass modified with AuNPs.

The morphologies of synthesized AuNPs as well as that of LbL films and capsules were investigated by AFM and TEM.

Steady-state emission and Fluorescence Lifetime Imaging Microscopy (FLIM) were used to study and compare plasmonic effects on phthalocyanine emission taking into account the different system's geometries.

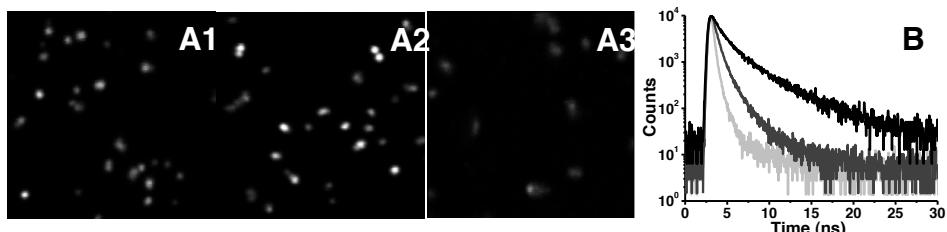


Figure 1. Confocal microscopy images of LbL nanocapsules coated with a lipid bilayer containing AlPcS_1 : **A1** – 3 layers of PAH/PSS; **A2** – 5 layers of PAH/PSS; **A3** – 7 layers of PAH/PSS. **B** – Fluorescence lifetime decays of A1 (gray); A2 (dark gray); and A3 (black).

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PS-60 – Chlorophyll-a as a Sensor of DMPC-DTAC-Water System*R. F. Correia, M. I. Viseu, S. M. Andrade**Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,
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The high efficiency of the light-harvesting processes in nature has inspired researchers on the study of photosynthetic pigments, especially chlorophyll-*a* (Chl-*a*). In this way, bio-inspired materials for use in solar cells or artificial leaves have been produced. However, chlorophyll molecules in the living photosynthetic organisms are in highly complex aggregated states, which are difficult to study.

Being able to change the Chl-*a* organization by compartmentalizing it in their hydrophobic/hydrophilic micro-environment, micelles and vesicles incorporating this pigment have been frequently used as models of thylakoid membranes.

In this work vesicles and several types of micelles, formed spontaneously during the solubilization of DMPC liposomes by the cationic detergent DTAC, were labeled with Chl-*a*. These colloidal structures, incorporating Chl-*a* in different aggregation and organization states, were studied by UV–Visible absorption, steady-state and time-resolved fluorescence, fluorescence correlation spectroscopy (FCS), and fluorescence lifetime imaging microscopy (FLIM).

In particular, Chl-*a* monomers and aggregates were detected by time-resolved emission; and their distribution in the giant colloidal structures (pure and mixed liposomes and threadlike micelles) was visualized by FLIM, Figure 1.

The colloidal structures found are in good agreement with our previous results of DSC [1] and DLS (unpublished work). Therefore, Chl-*a* can be used as a sensor of the DMPC–DTAC colloidal assemblies.

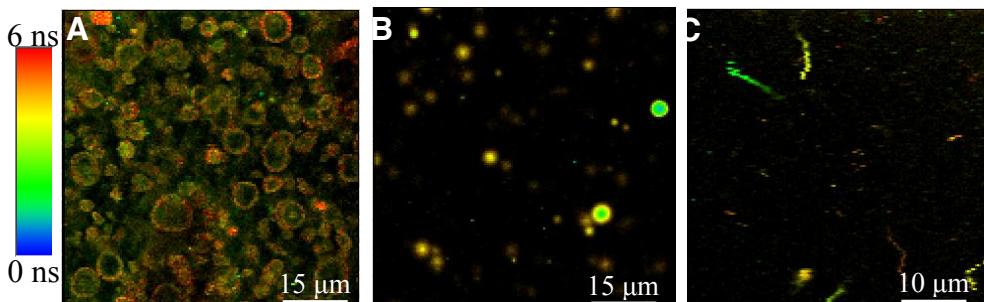


Figure 1. FLIM images of Chl-*a* inserted in: (A) DMPC liposomes; (B) DTAC–DMPC liposomes and (C) DTAC–DMPC threadlike micelles.

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PS-61 - Fluorescence quenching of L-cysteine capped CdTe quantum-dots by Cu(II)

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The special spectroscopic features of semiconductor nanoparticles (QDs) including high photostability, size tunability of luminescence, narrow emission and broad excitation spectra, etc., have made possible to avoid some of limitations of many organic fluorophores in the study of biological systems [1]. In spite of the extensive use of QDs as fluorescent labeling for biomolecules only recently some nanocrystals are used as fluorescence-based nano-sensors for physiologically relevant cations [2,3].

Copper is one of the elements which play an essential key role in the biochemistry of the human organism. Both excessive copper intake and copper deficiency lead to several disorders [4a, 4b]. It has been reported that Cu²⁺ ions selectively quench the CdTe QDs fluorescence with a minimal interference of other ions [5]. This circumstance allows an accurate determination of Cu²⁺ ions in submicromolar range with a possible application to the assessment of copper deficiency in healthy and ill people.

In this work L-cysteine capped CdTe nanoparticles were synthesized according to a hydrothermal method reported elsewhere [6]: Cd(NO₃)₂.4H₂O was dissolved along with L-cysteine hydrochloride in bidistilled water. The pH of the solution was adjusted to > 11.4 by adding NaOH solution. The reaction mixture was degassed with argon for 30-60 min. To this solution, freshly prepared, NaHTe solution (by reducing H₂TeO₄.2H₂O in bidistilled water using excess NaBH₄) was added. The reaction mixture was refluxed at 108 °C for 25 min. The crystal growth was arrested by leaving the reaction mixture at the room temperature.

The advantages, coming from the simplicity of the synthesis method and the high solubility in water of L-cysteine capped CdTe nanoparticles, are limited by some instability which affects to the nanocrystals fluorescence response. We have studied the experimental conditions needed to preserve the CdTe QDs fluorescence in order to perform Cu²⁺ determination in a suitable range.

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