XIV ELAFOT

Viña del Mar, Chile, november 11^{th}-14^{th}, 2019

XIV ELAFOT PROGRAM

Monday (Nov 11th)		Tuesday (Nov 12th)		Wednesday (Nov 13th)		Thursday (Nov 14th)	
		09:00 – 09:40	P2 Jayaraman Sivaguru	09:00 – 09:40	P5 Mauricio Baptista	09:00 – 09:40	P8 Gonzalo Cosa
		09:40 – 10:10	I1 Frank Quina	09:40 – 10:10	I4 José Robinson	09:40 – 10:00	O9 R. M. Wilson
		10:10 – 10:30	O1 Val Vullev	10:10 – 10:30	O6 Danilo Jara	10:00 – 10:15	ST3 M. Belén Rivas Aiello
		10:30 – 11:00	Coffee break	10:30 – 11:00	Coffee break	10:15 – 10:30	
						10:30 – 11:00	Coffee break
		11:00 – 11:40	P3 Rodrigo Palacios	11:00 – 11:40	P6 Raquel Galián	11:00 – 11:40	P9 Malcom Forbes
		11:40 – 12:10	I2 Felipe Avila	11:40 – 12:10	I5 Claudia Turro	11:40 – 12:10	I7 Andrés Thomas
		12:10 – 12:30	O2 Ricardo Matute	12:10 – 12:30	O7 Rodolfo I. Teixeira	12:10 – 12:30	Closing remarks
14:00 – 17:00	Registration (Sporting Club Viña del Mar)	12:30 – 14:30	Lunch, Poster Session 1	12:30 – 14:30	Lunch, Poster Session 2		
		14:30 – 15:00	I3 Cornelia Bohne	14:30 – 15:10	P7 Michael J. Davies		
		15:00 – 15:20	O3 Sylvia Braslawsky	15:10 – 15:40	I6 Claudio Borsarelli		
		15:20– 15:40	O4 M. Laura Dántola	15:40 – 16:00	08 Virginie Lhiaubet		
17:00 – 18:00	P1 Miguel García Garibay (Sporting Club Viña del Mar)	15:40– 16:10	Coffee break	16:00 – 16:30	Coffee break		
		16:10 – 16:50	P4 Gabriela Lagorio	16:30 – 16:45	ST1 Jael R. Neyra Recky		
		16:50 – 17:10	O5 Carolina Lorente	16:45 – 17:00	ST2 María José Sosa		
18:00 – 20:00	Welcome Reception (Sporting Club Viña del Mar)					19:00 – 22:00	Banquet (Sporting Club Viña del Mar)

P: Plenary (35 min + 5 min)
I: Invited Lecture (25 + 5 min)
O: Oral Presentation (15 + 5 min)
ST: Short Talk (10 min)

XIV ELAFOT

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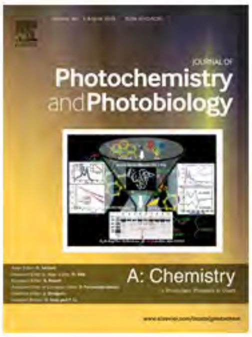
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FULL PROGRAM

Monday, Nov 11th "Sporting Club Viña del Mar – Salón Jackson"

14:00 – 17:00	**Registration**
17:00 – 18:00	**Opening Plenary Lecture P1:** Miguel García Garibay (University of California, Los Angeles, USA), "Photochemical Aspects of Crystalline Molecular Machines"
18:00 – 20:00	**Welcome Reception**

Tues*day*, Nov 12th

SESSION 1.

9:00 – 9:40	**Plenary Lecture P2:** Jayamaran Sivaguru (Bowling Green State University, Bowling Green USA), "Designing chromophores to uncover novel excited state reactivity"
9:40 – 10:10	**Invited Lecture I1:** Frank H. Quina (Universidade de São Paulo, São Paulo, Brazil), "Fruit, Flower and Wine Inspired Fluorescent Chromophores"
10:10 – 10:30	**Oral Presentation O1:** Val Vullev (University of California, Riverside, USA), "Fluorescent Nitropyrenes and Other Unusual Phenomena in Photochemistry"
10:30 – 11:00	Coffee Break

SESSION 2.

11:00 – 11:40	**Plenary Lecture P3:** Rodrigo Palacios (Universidad Nacional de Río Cuarto, Río Cuarto, Argentina), "Understanding and Designing Conjugated Polymer Nanopartices for Practical Applications"
11:40 – 12:10	**Invited Lecture I2:** Felipe Avila (Universidad de Talca, Talca, Chile.), "3-Hydroxykynurenine bound to eye lens proteins induces oxidative modifications in crystalline proteins through a type I photosensitizing mechanism"
12:10 – 12:30	**Oral Presentation O2:** Ricardo Matute (Universidad Bernardo O'Higgins, Santiago, Chile), "Non-RRKM Dynamics, Excited-State Aromaticity, and Regioselectivity on the Mechanism of the Triplet Di-π-Methane Rearrangement"
12:30-14:30	**LUNCH and 1st POSTER SESSION (odd numbers)**

SESSION 3..In Honor of Enrique San Roman Chairman: Sylvia Braslavsky

14:30 – 15:00	**Invited Lecture I3:** Cornelia Bohne (University of Victoria, Victoria, Canada), "Understanding complexity: Effect of Cations and Guest Size on the Cucurbit[7]uril-Guest Dynamics"
15:00 – 15:20	**Oral Presentation O3:** Sylvia Braslavsky (Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany), ".In memoriam Enrique San Román (1945-2019)"

15:20 – 15:40	**Oral Presentation O4:** Laura Dántola (Universidad Nacional de la Plata, La Plata, Argentina), “Type I photosensitization of Ubiquitin leads to fluorescent adduct formation, cleavage and dimerization”
15:40 – 16:10	Coffee Break

SESSION 4

16:10 – 16:50	**Plenary Lecture P4:** María Gabriela Lagorio (Universidad de Buenos Aires, Buenos Aires, Argentina), “Modeling light interaction with biological entities”
16:50 – 17:10	**Oral Presentation O5:** Carolina Lorente (Universidad Nacional de La Plata, La Plata, Argentina), “Antioxidant action of Resveratrol in the prevention of guanine photosensitized oxidation”

Wednesday, Nov 13th

SESSION 5.

9:00 – 9:40	**Plenary Lecture P5:** Mauricio Baptista (Universidade de São Paulo, Sao Paulo, Brazil), “Photodamage precision of photosensitized oxidations”
9:40 – 10:10	**Invited Lecture I4:** José Robinson-Duggon (Universidad de Panamá, Panamá,), ”Biosupramolecular Assemblies of Photosensitizer, Cucurbit[7]uril and Human Serum Albumin and their Phototoxic Effect in HeLa Cells Cultivated in vitro”
10:10 – 10:30	**Oral Presentation O6:** Danilo Jara (Universidad Andrés Bello, Viña del Mar, Chile), “A Cyrhetrenyl Acylhydrazone Photoswitch: Synthesis, Characterization and Singlet Oxygen Generation”
10:30 – 11:00	Coffee Break

SESSION 6.

11:00 – 11:40	**Plenary Lecture P6:** Raquel Galan (University of Valencia, Valencia, Spain), ”Colloidal semiconductor nanocrystals: Perovskite Shine Bright”
11:40 – 12:10	**Invited Lecture I5:** Claudia Turro (The Ohio State University, Columbus, Ohio, USA), “New Complexes with Extended Red Absorption for Photoinduced Drug Delivery”
12:10 – 12:30	**Oral Presentation O7:** Rodolfo I. Texeira (Federal University of Rio de Janeiro, Rio de Janeiro, Brazil.), “Ruthenium-functionalized Silica as Heterogeneous Photocatalysts”
12:30-14:30	**LUNCH and 2nd POSTER SESSION (even numbers)**

SESSION 7.

14:30 – 15:10	**Plenary Lecture P7:** Michael J. Davies (University of Copenhagen, Copenhagen, Denmark), “Photodamage precision of photosensitized oxidations. UV oxidation of cyclic AMP receptor protein, a global bacterial gene regulator, decreases DNA binding and cleaves DNA at specific sites, as a consequence of protein modification”

15:10 – 15:40	**Invited Lecture I7:** Claudio D. Borsarelli ((Universidad Nacional Santiago del Estero, Santiago del Estero, Argentina), "Functionalized hollow microcapsules built by multilayer self-assembly of photo-activatable polyelectrolytes"
15:40 – 16:00	**Oral Presentation O8:** Virginie Lhiaubet-Vallet (Universitat Politècnica de València, Valencia, Spain), "Sunscreen-Based Photocages for Topical Drugs"
16:00 – 16:30	Coffee Break

SESSION 8.

16:30 – 16:45	**Short Talk S1:** Jael R. Neira Recky (Universidad Nacional de La Plata, La Plata, Argentina), "New approach on Tyrosine photosensitized oxidation mechanism"
16:45 – 17:00	**Short Talk S2:** María José Sosa (Universidad Nacional de La Plata, La Plata, Argentina), "Characterization and membrane affinity of decyl-lumazines"

Thursday, Nov 14th

SESSION 9.

9:00 – 9:40	**Plenary Lecture P8:** Gonzalo Cosa (McGill University, Quebec, Canada), "Chemi-controlled Activation of Fluorescent Probes in Imaging and Phototherapies"
9:40 – 10:00	**Oral Presentation O9:** R.M. Wilson (Bowling Green State University, Bowling Green, Ohio, USA), "Dihydrodioxin Photochemistry as a Tool in DNA Cleavage
10:00 – 10:15	**Short Talk S3:** María Belen Rivas (Universidad Nacional de La Plata, La Plata, Argentina), "Study of spectroscopy properties of carbon nitride quantum dots"
10:15 – 10:30	
10:30 – 11:00	Coffee Break

SESSION 10.

11:00 – 11:40	**Plenary Lecture P9:** Malcolm D. E. Forbes (Bowling Green State University, Bowling Green, USA), "Photons, Radicals, Bubbles and Beer: Using Photochemistry and Electron Paramagnetic Resonance Spectroscopy to Understand the Universe"
11:40 – 12:10	**Invited Lecture I8:** Andrés Thomas (Universidad Nacional de La Plata, La Plata, Argentina.), "Tyrosine dimer: when an oxidative lesion of proteins is able to photosensitize further damage"
12:10 – 12:30	**Closing Remarks**
19:00-22:00	**Banquet "Sporting Club Viña del Mar – Salón Derby"**

PLENARY

TALKS

Abstracts

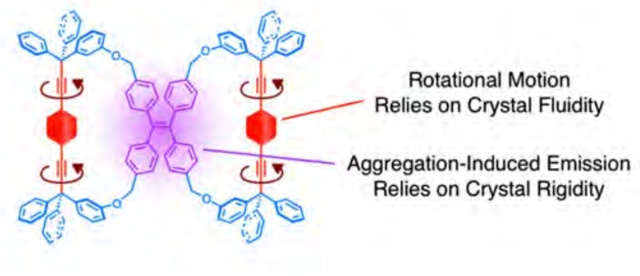
Monday 11th, 17:00-18:00

Photochemical Aspects of Crystalline Molecular Machines

Morgan Howe, Miguel A. Garcia-Garibay

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569 USA

Crystalline molecular machines rely on architectures based on a combination of static and rapidly moving components that are able to respond individually and collectively to external stimuli. Among them, molecular rotors are expected to have functions that rely on units designed to rotate or reorient in response to external electric or magnetic fields, and to display field-induced birefringence, dichroism, second-order non-linear optical responses, and other addressable physical properties. Additional strategies to control the frequency of internal rotation and the physical response of crystalline molecular machines are based on the use photochemical changes that affect their internal structure. This presentation will illustrate the development of these concepts as a result of considering the relation between dynamics and order in condensed phase matter, their realization using several structural platforms, some of the tools used to determine solid state rotational dynamics, and examples where we explore the potential of various photochemical processes.



Tuesday 12th, 9:00-9:40

Designing chromophores to uncover novel excited state reactivity

Jayaraman Sivaguru*

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Uncovering new excited state reactivity provides opportunities to build complex molecular architectures often with unique stereochemistry. A fundamental challenge in such a process involves controlling excited state reactivity of organic molecules due to the short lifetimes of the reactive species leading to stereo-enriched products. We have been interested in developing strategies for controlling the stereochemistry of products where the reactants reach the excited state(s) upon UV and/or visible light irradiations. This presentation will highlight our methodology of employing UV and/or visible light for performing photoreactions with excellent control over reactivity and selectivity. Based on photochemical and photophysical investigations, the presentation will highlight novel excited state reactivity of organic molecules, how to influence their excited state behavior towards productive reaction pathways and provide a mechanistic rationale for the observed reactivity in different systems.[1-4]

References

(1) Ahuja, S.; Raghunathan, R.; Kumarasamy, E.; Jockusch, S.; Sivaguru, J. Realizing the Photoene Reaction with Alkenes under Visible Light Irradiation and Bypassing the Favored [2 + 2]-Photocycloaddition *J. Am. Chem. Soc.*, **2018**, *140*, 13185–13189.

(2) Kumarasamy, E.; Kandappa, S.; Raghunathan, R.; Jockusch, S.; Sivaguru, J.* Realizing Aza Paternò-Büchi reaction" *Angew. Chem. Int. Ed.* **2017,** 56, 7056 –7061. *(Frontispiece).*

(3) Kumarasamy, E; Raghunathan, R.; Jockusch, S.; Sivaguru, J.* Transposed Paternò-Büchi Reaction *J. Am. Chem. Soc.*, **2017**, *139*, 655–662.

(4) Kumarasamy, E; Ayitou, A. J. -L.; Vallavoju, N.; Raghunathan, R.; Iyer, A.; Clay, A.; Kandappa, S.; Sivaguru, J.* Tale of Twisted Molecules: Taming Asymmetric phototransformations through non-biaryl atropisomers. *Acc. Chem. Res.* **2016**. 49, 2713−2724.

Tuesday 12th, 11:00-11:40

Understanding and Designing Conjugated Polymer Nanopartices for Practical Applications

<u>Rodrigo E. Palacios</u>

Universidad Nacional de Río Cuarto, Dto. Química, FCEFQyN. Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados (IITEMA), UNRC-CONICET. Río Cuarto 5800, Córdoba, Argentina. e-mail: rpalacios@exa.unrc.edu.ar [1]

Conjugated polymers (CPs) are organic semiconductors of great relevance due to their application in organic-electronic devices, such as solar cells, light emitting diodes, and field effect transistors, among others. It is generally accepted that electronic excitations in CPs are localized in relatively short segments (5-12 monomers) called quasi-chromophores that act largely independently, so that a polymer chain can be considered as a multicromophoric system. The performance of CP-based devices depends, to a large extent, on elementary photoinduced energy transfer (ET) processes that occur between these quasi-chromophores and dopants or impurities present in the polymer matrix. In particular, the efficiency of ET from CP to dopant is associated with a benchmark parameter named Antenna Effect (AE). Conjugated polymer nanoparticles (CNP) are nanostructured systems that can be manufactured controlling particle size as well as the amount and spatial distribution of dopant dyes. This allows their use as model systems for the study of confined ET processes and also for their use in a series of practical applications that critically depend on the AE.

In this talk I will describe our work in the development of doped CNP and in the characterization of intraparticle ET processes using conventional spectroscopic techniques, measurements of single particle fluorescence and computational modeling. Through the modeling of experimental measurements, the influence of several parameters on the ET process and on the AE was determined, such as: quantity and location of dopants and traps, exciton diffusion length and particle size. (1) The knowledge obtained allowed the optimization of CNP for applications where efficient photoexcitation of "photoactive" molecules is required. To discuss some applications of these materials I will summarize our work in the development of CNP as efficient photosensitizers of reactive oxygen species (2) and their successful use in photodynamic therapy protocols against brain and colorectal cancer cells (3) and in photodynamic inactivation of antibiotic-resistant bacteria of clinical relevance (4). Finally, I will describe our recent work using CNP as efficient macro-photoinitiators of vinyl polymerization to form biocompatible macro and nano hydrogels in aqueous media in the absence of co-initiators.

References:
1) Ponzio, R.A. et al. *J. Phys. Chem. C.* To be submitted (2019).
2) Spada, R. M. et al. *Dyes Pigments*. 149, 212–223 (2018).
3) Ibarra, L. E. et al. *Nanomed.* 13, 605–624 (2018).
4) Martinez, S.R. et al. *ACS Infectious Diseases.* To be submitted (2019).

Plenary Lecture P4

Tuesday 12th, 16:10-16:50

Modeling light interaction with biological entities

María Gabriela Lagorio[1,2]

[1]CONICET, Universidad de Buenos Aires, INQUIMAE, Facultad de Ciencias Exactas y Naturales, Buenos Aires, Argentina.[2]Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Dpto. de Química Inorgánica, Analítica y Química Física, Ciudad Universitaria. Pabellón II, 1er piso, C1428EHA, Buenos Aires, Argentina. e-mail: mgl@qi.fcen.uba.ar

Our research interest is focused on studying the interaction of light with biological entities in order to get information about the system in a non-destructive way.

These systems usually present two special features: high concentration of chromophores and high light scattering. From a spectroscopic and photophysical point of view, these peculiarities introduce some complexity in their study. Because of this, the accurate modelling of the interaction is usually necessary to avoid artifacts and to comprehend the processes that take place.

In this talk, I will present some of our contributions in this area. They range from the development of theoretical approaches to the implementation of applied methodologies.

I will describe physical models used in the analysis of chlorophyll fluorescence in leaves and canopy with application in remote sensing [1, 2], optical methodologies for food control [3- 4] and quantification of fluorescence *in vivo* for evaluation of its relevance as a biosignal [5-7].

Acknowledgments The University of Buenos Aires, Agencia Nacional de Promoción Científica y Tecnológica and CONICET are acknowledged for financial support.

References

[1] Cordon, G. B.; Lagorio, M. G. Photochem. Photobiol. Sci., 2006, 5, 735–740
[2] Romero, J.M; cordon, G. B.; Lagorio, M. G. Rem Sens Environ, 2018, 204, 138-–146
[3] Ospina Calvo, B.; Parapugna T. L.; Lagorio, M. G. Photochem. Photobiol. Sci., 2017, 16, 711–710
[4] Mendes Novo, J; Iriel, A.; Lagorio, M. G. Photochem. Photobiol. Sci., 2012, 11, 724–730
[5] Lagorio, M. G.; Cordon, G. B.; Iriel, A. Photochem. Photobiol. Sci., 2015, 14, 1538–1559
[6] Barreira, A. S.; Lagorio, M. G.; Lijtmaer, D. A.; Lougheed, C; Tubaro, P. L. J. Zoology, 2012, 288, 135–142
[7].Taboada, C; Brunetti, A. E.; Pedron, F. N. ; Carnevale Neto, F.; Estrin, D. A.; Bari, S. E.; Chemes, L. B.; Peporine Lopes, N. ; Lagorio, M. G.; Faivovich, J. PNAS, 2017, 114, 3672–3677

Wednesday 13th, 9:00-9:40

Photodamage precision of photosensitized oxidations

Mauricio S. Baptista

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Photosensitized oxidations, which are reactions provoked by the interaction of light with photosensitizer (PS) molecules, are being used in medical technologies, such as photodynamic therapy, in order to trigger oxidation of biomolecules and consequently to eliminate cancer cells or pathogens. Damage in cytoplasmic or organelle membranes is key to modulate the mechanism as well as the overall efficiency of regulated cell death.[1,2] There are two major mechanisms of photosensitized oxidations, called type I and type II, representing respectively, the direct oxidation of biological targets (direct-contact reactions) and the oxidations mediated by diffusing species, such as singlet oxygen.[3] Nevertheless, the detailed molecular steps leading to biological injury remains largely uncharacterized and it is not clear how precise can be the spatial damage induced by the photosensitized oxidation reactions. In case of direct-contact reactions, the damage is performed precisely in the place where the excited species is generated and for type II processes, singlet oxygen or other diffusing species can carry oxidation potentials hundreds of nanometers or of micrometers away from the point of light absorption. In a recent publication, we demonstrated that for a PS to fully compromise membrane function, it needs to be sacrificed through contact-dependent reactions, forming lipid-truncated aldehydes, which are the active agents causing membrane leakage.[4,5] Therefore, relevant damage that definitively changes the outcome of cells are precisely the locus of PS location, and therefore, justifies the search for molecular-specific oxidation-induced photodamage. Also, PS regeneration should be exploited as an effective tool to maximize the effects of photosensitized oxidations.

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Wednesday 13th, 11:00-11:40

Colloidal semiconductor nanocrystals: Perovskite Shine Bright

Raquel E. Galian

Institute of Molecular Science, University of Valencia, c/ Catedrático José Beltrán 2, Paterna, Valencia, Spain. E-mail: raquel.galian@uv.es

Metal halide perovskites $APbBr_3$ ($A = CH_3NH_3^+$ or Cs^+; $X = Cl^-$, Br^-, I^-) are considered a revolutionary material in the photovoltaic community, which nowadays reach a power conversion efficiency value higher than 23 % after ten years from their first report. [1]

Perovskite nanocrystals present similarities with conventional semiconductors quantum dots (CdSe or CdTe) such as a wide absorption spectrum, narrow emission peak, high absorption coefficient and size-dependent electronic properties. However, they can be synthesized with high photoluminescence quantum yield without any electronic passivation due to their defect-tolerance. [2]

We have prepared for the first time colloidal perovskites nanocrystals in 2014, using a medium length organic ligand (octylammonium bromide) in octadecene at 80 ^{0}C to confine the material into the nanoscale, with a luminescence quantum yield of 20%. [3] Since then, different strategies were developed to produce highly luminescent colloidal perovskites up to 100 % according with the nature of the organic capping and the molar ratio between the precursors. [4] The progress in the synthetic methodologies (bottom-up and top-down) and the key role of the organic capping in their emissive properties will be presented. Moreover, different applications of colloidal perovskites (Figure 1), such as preparation of conductive thin film and electroluminescent devices, design of low dimensional perovskite nanomaterials and photocatalysis will be discussed. [5]

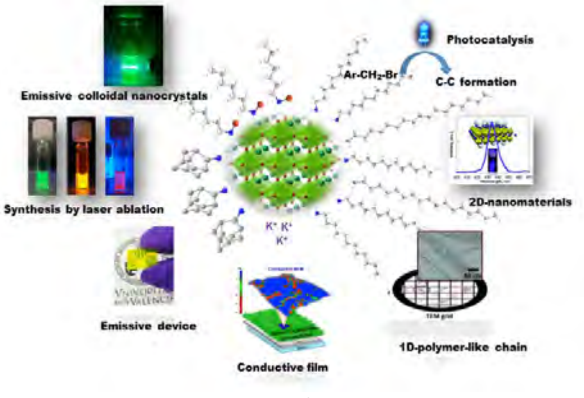

Figure 1: Synthesis and applications of colloidal perovskite nanocrystals.

References

[1] a) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050; b) A. K. Jena, A. Kulkarni, T. Miyasaka, *Chemical Reviews* **2019**, 119, 3036.

[2] a) V. S. Chirvony, S. González-Carrero, I. Suárez, R. E. Galian, M. Sessolo, H. J. Bolink, J. P. Martínez-Pastor, J. Pérez-Prieto, *J. Phys. Chem. C* **2017**, 121, 13381; b) D. Meggiolaro, S. G. Motti, E. Mosconi, A. J. Barker, J. Ball, C. Andrea Riccardo Perini, F. Deschler, A. Petrozza, F. De Angelis, *Energy & Env. Sci.* **2018**, 11, 702.

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Plenary Lecture P7

Wednesday 13th, 14:30-15:10

Photodamage precision of photosensitized oxidations

UV oxidation of cyclic AMP receptor protein, a global bacterial gene regulator, decreases DNA binding and cleaves DNA at specific sites, as a consequence of protein modification

Fabian Leinisch [1], Michele Mariotti [1], Søren Lindemose [2], Sofie Hagel Andersen [2], Per Hägglund [1], Niels-Erik Møllegaard [2], Michael J. Davies [1]

Dept. of Biomedical Sciences[1]and Dept. of Cellular and Molecular Medicine[2], Panum Institute,
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UV light is a widely-employed, and environmentally-sensitive bactericide but its mechanism of action is not fully defined. Proteins are major chromophores in many cells and are significant targets for damage due to their abundance. In *E. coli* (and other Gram-negative bacteria) the cyclic AMP receptor protein (CRP / CAP) is known to regulate more than 500 genes. In this study we have examined the mechanisms and consequences of exposure of isolated dimeric CRP-cAMP to UVA and UVB light, and how this modified both the protein in isolation and its complex with DNA.

It is shown that UV exposure can modify specific Met, Trp, Tyr, and Pro side-chains on the CRP protein (as detected by amino acid analysis and mass spectrometry peptide mass mapping), generates specific inter-protein Tyr63-Tyr41 cross-links (detected using a $H_2{}^{18}O$ mass spectrometry labelling approach), and decreases DNA binding via oxidation of pairs of Met114/Pro110 residues. The latter pairs of residues are located in close proximity at the CRP dimer interface, with oxidation affecting the interaction of the protein monomers.

UV exposure also modifies DNA-bound cAMP-CRP, with this resulting in DNA cleavage at specific G/C residues within the DNA sequence bound to the CRP. Oxidation of the protein also increases CRP dissociation from bound DNA as a result of changes to the protein structure. The modifications formed at the CRP dimer interface (Met114/Pro110), and the DNA strand cleavage (which occurs in close proximity to Met189) are proposed to occur via oxidation of the Met residues to reactive persulfoxides. These data suggest that UV-induced modification of CRP contributes to the UV sensitivity of some bacteria.

Plenary Lecture P8

Thursday 14th, 9:00-9:40

Chemi-controlled Activation of Fluorescent Probes in Imaging and Phototherapies

Gonzalo Cosa

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Chemoselective fluorogenic probes rely on the induction/enhancement of fluorescence upon activation of an otherwise dimly emissive fluorophore in the presence of a chemical cue [1]. A number of photophysical/photochemical processes may be exploited in designing this type of probes, where judicious choice of the mechanism may enable monitoring real-time in a non-invasive manner where and when reactive intermediates are formed, thus enabling reaction screening in e.g. biological settings. Provided the probes are capable of undergoing order of magnitude fluorescence enhancements following interception of target intermediates, and by applying concepts of single molecule localization microscopy (SMLM) [2], one may be able to count and report single events.

Our ongoing interest on the role of lipid peroxidation and associated byproducts - including lipid derived electrophiles (LDEs) - in cellular physiology and pathology have led to developing a number of fluorogenic probes over the years intended to monitor lipid peroxyl radicals, electron transport in membranes, and how LDE react and evolve within cells. In this presentation I will describe our progress on the preparation of various types of fluorogenic probes relying on modified BODIPY dyes. I will discuss the mechanism of action of the probes providing a rationale for the choices of trap and reporter (BODIPY dyes) segments on the basis of signal sensitivity (and the ensuing photo-physical -chemical processes), chemical selectivity and environment specificity [3]. I will provide recent examples for the use of the probes in bio-analytical assays and in state-of-the-art fluorescence imaging studies including super resolution imaging based on SMLM [3] of reactions in biological milieu [3e].

I will also briefly introduce new directons, extending the paradigm of activatable probes beyond fluorescence, showing that other photophysical or photochemical properties may be activated following a reaction of interest. In particular, we will show how singlet oxygen photosensitization may be activated following a redox reaction at the trap segment of a sensitizer in what constitutes an autocatalytic activation of $^1O_2$ sensitization. The implications to cellular probing will be illustrated [4].

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Plenary Lecture P9

Thursday 14th, 11:00-11:40

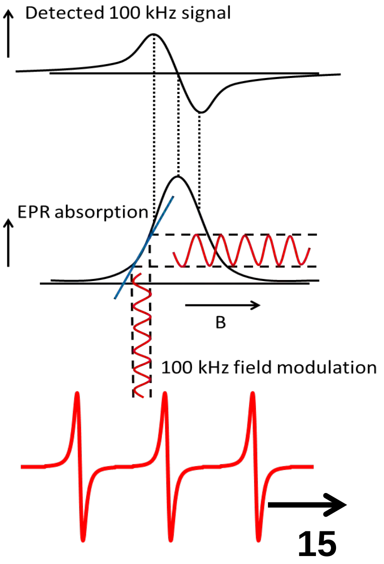
Photons, Radicals, Bubbles and Beer: Using Photochemistry and Electron Paramagnetic Resonance Spectroscopy to Understand the Universe

Malcolm D. E. Forbes

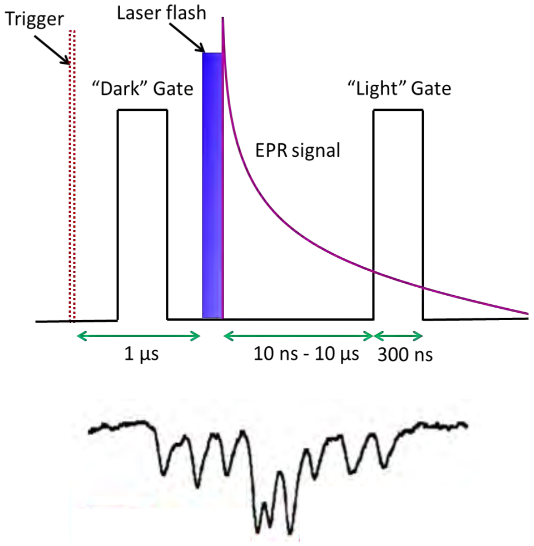
Director, Center for Pure & Applied Photosciences
Professor of Chemistry
Bowling Green State University

Our laboratory has a long-standing interest in the structure, reactivity, and dynamics of free radicals in both homogeneous and heterogeneous media. In this lecture, the basic tenets of steady-state and time-resolved (CW) electron paramagnetic resonance spectroscopy (SSEPR and TREPR) are explained, and their use in understanding the physical and chemical behavior of free radicals is outlined. Examples to be presented include the use of stable nitroxide spin probes to investigate the drying and curing of architectural coatings, and to probe the physical properties of structured (non-Newtonian) fluids at the molecular level. Chemical reactivity involving free radicals can be studied directly using TREPR, for example in the study of the mechanism for the lightstruck flavor (so-called "skunking") of beer. Reactivity can also be investigated using spin trapping techniques. Two different trapping methods will be presented: nitrones can be used to confirm the mechanism of action of biocompatible polymer initiators, and the reaction of hindered amines with singlet oxygen can be used to quantify the kinetics and topology of such reactions in confined media. Finally, the application of EPR spectroscopy to study two aspects of polymer chain dynamics in liquid solution will be presented: 1) main chain radicals of acrylic polymers studied as a function of polymer structure and temperature, and 2) long-range radical-triplet state pair interactions in acrylic polymers.

Steady-state EPR



Time-Resolved (CW) EPR



INVITED

LECTURES

Abstracts

Invited Lecture I1

Tuesday 12th, 9:40-10:10

Fruit, Flower and Wine Inspired Fluorescent Chromophores

Frank H. Quina[1], Cassio P. Silva[1], Gustavo T. M. Silva[1], Karen M. Silva[1], Adilson A. Freitas[2], Farhan Siddique[3], Xue Li[3], Juanjuan He[3], Adelia J. A. Aquino[3]

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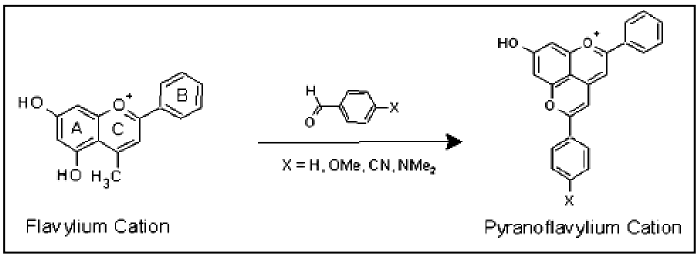
The colors of anthocyanins, the natural plant pigments responsible for most of the red, purple and blue colors of flowers, fruits and leaves, are modulated by pH, substitution and complexation with metal ions and/or colorless organic molecules (copigments) [1]. Anthocyanins (and analogous synthetic flavylium cations) are very efficient at absorbing and dissipating light energy, which enhances their photostability but makes them less interesting as chromophores in practical applications. During the maturation of red wine, the anthocyanins of grapes are transformed into pyranoanthocyanins, which have a pyranoflavylium cation chromophore [1]. The relatively facile synthesis of substituted pyranoflavylium cations permits manipulation of the redox properties and the nature of the lowest excited state (TICT, charge-transfer or localized) [2]. This excited state character, together with absorption spectra and excited state energies, can be nicely reproduced by *ab initio* quantum chemical calculations (ADC(2) combined with COSMO simulation of solvent environments), facilitating the rationalization of the observed photophysical behavior and the design of new falvylium and pyranoflavylium cation derivatives.



Unlike the natural pigments, synthetic flavylium and pyranoflavylium cations can be quite fluorescent. In contrast to anthocyanins and flavylium cations, pyranoflavylium cations form long-lived triplet states and singlet oxygen [3], and show reversible redox behavior and large two-photon absorption cross sections [4]. By circumventing the ultrafast energy dissipation pathways that contribute to the photostability of their natural pigment analogs, synthetic pyranoflavylium cations serve as a convenient chromophoric moiety for the rational design of fluorescent pigments [5], novel PDT sensitizers [4] and photoredox catalysts.

References:

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Acknowledgment: Financial and fellowship support from CNPq and CAPES (Finance Code 001) is gratefully acknowledged.

Invited Lecture I2

Tuesday 12th, 11:40-12:10

3-Hydroxykynurenine bound to eye lens proteins induces oxidative modifications in crystalline proteins through a type I photosensitizing mechanism

Felipe Ávila[1], Natalia Ravello[1], Antonio L. Zanocco[2], Luke F. Gamon[3], Michael J. Davies[3] and Eduardo Silva[4].

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[4]*Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile*

Photosensitized reactions mediated by endogenous chromophores have been associated with the etiology of age-related cataract disease. Endogenous chromophores such as 3-hydroxykynurenine (3OHKN) can be found in both free form and bound to crystallin proteins. However, their efficiency in generating photo-induced oxidative modifications on eye lens proteins is not completely understood. In this work, the efficiency and photodynamic activity of 3OHKN bound to both lysine (3OHKN-Lys) and bovine lens proteins (3OHKN-BLP) was assessed and compared with the photosensitizing activity of the major chromophore arising from glucose degradation (GDC). The photosensitizing activity of 3OHKN-Lys, 3OHKN-BLP and GDC was characterized by measurement of singlet oxygen quantum yields, O_2 consumption, SDS-PAGE and amino acid analysis of the photo-oxidized proteins. Singlet oxygen quantum yields under 20% O_2 atmosphere were 0.02, 0.01, and 0.27 for 3OHKN-Lys, 3OHKN-BLP and GDC, respectively. O_2 consumption by photosensitized reactions was more efficient for 3OHKN-BLP, with the extent of O_2 consumption being ~28% higher than for 3OHKN-Lys and GDC under both 5 and 20% O_2. SDS-PAGE showed that protein crosslinking is dependent on the O_2 concentration, and more extensive at 5 than 20% O_2. GDC and 3OHKN-Lys were the most efficient crosslinkers at 20 and 5% O_2, respectively. Amino acid analysis of the irradiated proteins showed consumption of Trp, His, Tyr and Phe, and formation of kynurenine (from Trp), methionine sulfoxide (from Met) and DOPA (from Tyr). Kynurenine formation was dependent on the O_2 concentration with higher amounts detected at 5 than 20% O_2 for 3OHKN-BLP and 3OHKN-Lys, with 3OHKN-BLP the most efficient sensitizer. Our results suggest that 3OHKN-BLP can elicit photo-oxidative damage mainly by a type I photosensitizing mechanism, with this likely to be the most prevalent pathway at the low physiologic O_2 concentrations in the eye lens.

Invited Lecture I3

Tuesday 12th, 14:30-15:00

Understanding complexity: Effect of Cations and Guest Size on the Cucurbit[7]uril-Guest Dynamics

Kevin A. Vos, Christie Lombardi, Elisa Medeiros dos Santos, Sree G. Talluri, Suma S. Thomas, David J. Berg and Cornelia Bohne*

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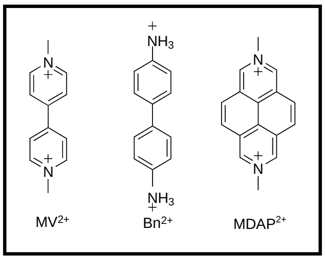
Increased complexity in chemical systems provides an opportunity to achieve multiple and different outcomes for these systems. The application for functional materials of emergent properties from complex behavior is one of the incentives for the development of systems chemistry.[1] Studies of supramolecular dynamics provides an understanding on how competitive kinetic pathways lead to different mechanistic outcomes in the formation of host- guest complexes.

Cucurbit[7]uril (CB[7]) is a macrocycle that forms complexes with hydrophobic guests. High affinity CB[7]-guest complexes are formed for hydrophobic guests with positive charges. In addition, CB[n]s bind cations to the portals of the host cavity.

The binding of (1-(2-naphthyl)ethylammonium, NpH^+) was previously shown to occur to free CB[7].[2] The fast binding of cations led to the decrease of the free CB[7] concentration, slowing the guest binding dynamics to the millisecond time scale.[2] We show in this work that the ratio of guest to cation concentrations, as well as the nature of the cation, changes the binding mechanism and affects the host-guest dynamics. At low NpH^+ concentrations the guest forms an exclusion complex which competes with the binding of Na^+, leading to the observation of two relaxation processes. Changing the cation to Ca^{2+} led to the observation of three relaxation processes, where the additional process is due to the formation of the NpH^+@CB[7]•Ca^{2+} complex. This Ca^{2+} capped complex led to the slowdown of the guest. These results show that in systems containing different cations, such as biological media, the guest residence time inside a CB[n] will depend on the types of cations and their concentration ratios.

The binding dynamics for guests with different structures but similar equilibrium constants (10^7 M^{-1}) were compared. MV^{2+} was previously shown to have a fast binding dynamics with CB[8][8] and we confirmed this fast dynamics for CB[7] (< 1 ms). Moving the charges to substituents on the aromatic ring (Bn^{2+}) slowed the kinetics (~ 200 ms), and increasing the aromatic moiety ($MDAP^{2+}$) led to a further slowdown (~120 s). The change in dynamics by a factor of 10^5 can be used to design functional systems that will be responsive on different time scales.



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Invited Lecture I4

Wednesday 13th, 9:40-10:10

Biosupramolecular Assemblies of Photosensitizer, Cucurbit[7]uril and Human Serum Albumin and their Phototoxic Effect in HeLa Cells Cultivated *in vitro*

José Robinson-Duggon,[1,2] **Ana María Edwards**[1] **and Denis Fuentealba**[1]

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Photodynamic therapy (PDT) is a minimally invasive technique currently approved for the treatment of cancer, which is based on the irradiation of a photosensitizer, causing the generation of reactive oxygen (ROS), specially singlet oxygen ($^1O_2$), which are able to react with organic material and biomolecules, such as nucleic acids, lipids and proteins. Therefore, inducing the death of abnormal cells either through apoptosis, necrosis or autophagy [1]. Fatty acids derivatives were prepared with toluidine blue O (TBO^+), which has been used for the detection of malignant tissue, has shown some selectivity for cancer cells and it has low dark toxicity [2]. These derivatives were characterized by NMR and mass spectrometry. Also, their photophysical and photochemical properties were characterized by determining their fluorescence lifetime, triplet excited state lifetime and singlet oxygen quantum yield of each derivative. These derivatives were prepared in order to increase the hydrophobicity, and the affinity to human serum albumin (HSA), as well as, the incorporation within HeLa cells cultivated *in vitro*. These derivatives were encapsulated within cucurbit[7]uril (CB[7]), a pumpkin-like molecular container, to increase their phototoxicity, and to try to control their release. The formation of inclusion complexes with CB[7] were combined with the association with HSA, which possesses several binding sites for hydrophobic molecules, to form *biosupramolecular complexes* to try to improve the biodistribution, and bioaccumulation of the photosensitizers. The encapsulation inside CB[7] due to its host-guest interactions was able to increase the fluorescence intensity and the fluorescence lifetime, as well as, the generation of singlet oxygen. These are desirable properties for the detection *in vivo* in cancer tissue and to increase the phototoxicity in PDT [3-5]. Moreover, since HSA is the most abundant protein in the bloodstream and it has been used in pharmaceutical formulations for therapeutic applications, which take advantage of its long period of circulation and the enhanced permeability and retention that are present in the tumors for a targeted therapy [6]. We conducted incorporation, co-localization and phototoxicity experiments using HeLa cells cultivated *in vitro* to assess the performance of the photosensitizers when they were incorporated by the different drug delivery systems that formed these *biosupramolecular complexes* to describe its potential applications in PDT.

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Wednesday 13th, 11:40-12:10

New Complexes with Extended Red Absorption for Photoinduced Drug Delivery

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Light activation of a drug represents an important as mode of cancer therapy, in some cases superior to traditional treatments, due to its low levels of invasiveness and systemic toxicity. Inorganic complexes that undergo photoinduced ligand exchange will be presented, which have been used to release caged drugs and enzyme inhibitors with spatiotemporal control. In addition, some complexes were designed to also sensitize the production of 1O2. These complexes represent important systems whose reactivity can be initiated by light with potential applications in photochemotherapy (PCT). Various Ru(II) complexes will be presented, along with their activity towards biological targets and cancer cells. Importantly, Ru(II) complexes were recently discovered to undergo multiple photochemical pathways following activation with light, and this property was used to design new dual-action compounds. These new complexes are able to both release a medically relevant compound and to produce 1O2 and were shown to exhibit significant enhancement of activity stemming from their ability to induce cell death via two different, independent pathways. Complexes able to deliver pyridine as a model compound representing a caged drug will be discussed, along with observed excited state dynamics. New strategies developed for the photoinduced exchange of pyridine-containing drugs and their attachment to tumor-targeting antibodies will also be presented. Rh2(II,II) complexes that are able to produce 1O2 upon irradiation with visible light and are non-toxic in the dark represent a new class of agents for potential photodynamic therapy. The complexes presented provide a new platform for drug delivery and enhanced therapeutic activity upon excitation with low energy light.

Invited Lecture I6

Wednesday 13th, 15:10-15:40

Functionalized hollow microcapsules built by multilayer self-assembly of photo-activatable polyelectrolytes

Claudio D. Borsarelli

Instituto de Bionanotecnología del NOA (INBIONATEC). CONICET – Universidad Nacional Santiago del Estero. RN 9, km 1125. CP 4206, Santiago del Estero. Argentina

The fabrication of hollow microcapsules (HMC) with a polyelectrolyte shell assembled by the layer-by-layer (LbL) technique onto the surface of removable micro-templates has received large attention, because of their potential applications in diverse areas ranging from medicine and biotechnology, up to catalysis and synthetic chemistry. The properties and applications of the HMC can be tuned by selecting the micro-template that controls shape and size, polyelectrolyte nature for mechanical and interfacial characteristics, and additives occluded in the core and/or shell for specific functionality. Typical synthetic polyelectrolytes used for multilayer formation are sodium poly(styrene sulfonate) (PSS), poly(vinyl sulfate) (PVS); poly(ethylenimine) (PEI) and poly(allylamine hydrochloride) (PAH); among other biological polyelectrolytes such as DNA, chitosans, and proteins. The functionalization of the microcapsule shell can be obtained by decoration with organic dyes, metal nanoparticles, antigens, or using intrinsically functionalized polyelectrolytes.

Therefore, the functionalized HMC can be able to respond to external stimuli, such as pH, temperature, light, ionic strength, etc., generating specific responses for instance controlled release, molecular recognition and sensing, redox and photo-redox functions, among others.

Here, we present a couple of recent examples of functionalized HMC constructed using $CaCO_3$ microspheres as sacrificial template covered with photo-activatable polyelectrolytes such: **i**) DNA-bioinspired polymer grafting the vinylbenzylthymine (VBT) monomer between ionic units of sodium vinylphenylsulfonate (VPS) or vinylbenzyltriethylammonium chloride (VBA), which are able to crosslink through thymine dimers by UVB irradiation, controlling HMC mechanical stability and permeability; and **ii**) poly(allylamine hydrochloride) with covalent attached rose Bengal (PAH-RB) and sodium poly(styrene sulfonate) (PSS) as counter-polyelectrolyte to form HMC with singlet oxygen photosensitizing properties.

The presented results remark the versatility and suitability of HMC grafted with photo-activatable polyelectrolytes for its application in controlled release of occluded substrates and photo-oxidation reactions with a micro-sized photosensitizer easily removable and reusing in aqueous solutions.

Thursday 14th, 11:40-12:10

Tyrosine dimer: when an oxidative lesion of proteins is able to photosensitize further damage

Lara O. Reid, Mariana Vignoni, M. Laura Dántola, Andrés H. Thomas

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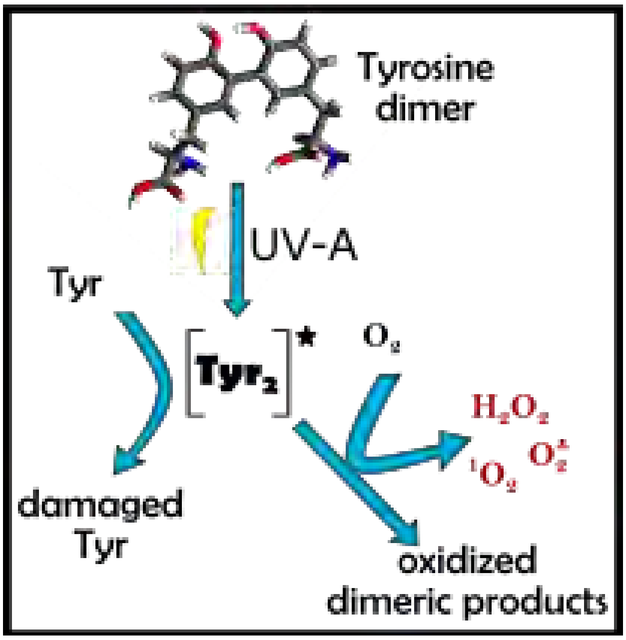
The tyrosine dimer (Tyr_2), a covalent bond between two tyrosines (Tyr), is one of the most important modifications of the oxidative damage of proteins. This compound is increasingly used as a marker of aging, stress and pathogenesis. At physiological pH, Tyr_2 is able to absorb radiation at wavelengths significantly present in the solar radiation and artificial sources of light. As a result, when Tyr_2 is formed *in vivo,* a new chromophore appears in the proteins. Despite the biomedical importance of Tyr_2, the information of its photochemical properties is limited due to the drawbacks of its synthesis.

We have optimized a simple, one-step method to synthesize Tyr_2, using pterin (Ptr) as a photocatalyst. Our procedure is carried out in aqueous solutions under UV-A radiation for few minutes. The purification of Tyr_2 is performed by reverse-phase chromatography. The highly pure obtained solution was used to deeper study its photochemical properties.

We have studied the photodegradation of the acid and alkaline form of Tyr_2 in aqueous solution under UV-B and UV-A radiation. In the absence of oxygen Tyr_2 is photostable. On the other hand, excitation in the presence of oxygen leads to the photodegradation of Tyr_2, yielding different products which conserve the dimeric structure. During its photodegradation different reactive oxygen species, like hydrogen peroxide, superoxide anion and singlet oxygen ($^1O_2$), are produced. The quantum yield of $^1O_2$ production is 0.15 ± 0.05, which is similar to that obtained for free Tyr. In addition, Tyr_2 is able to sensitize the photodegradation of Tyr.

This study indicates that when Tyr_2 is generated in a protein structure, an intrinsic potential photosensitizer is formed, extending the active fraction of light towards the UV-A range. Therefore a product of a photosensitized process can act as a photosensitizer itself leading to further photosensitized damage, thus amplifying the harmful effects of UV radiation on biological systems.



ORAL

PRESENTATION

Abstracts

Tuesday 12th, 10:10-10:30

Fluorescent Nitropyrenes and Other Unusual Phenomena in Photochemistry

Val Vullev,[1]

University of California, Riverside, CA 92521, U.S.A.[1]

The advent of organic electronics and photonics places high demands for synthetic conjugates with diverse variety of properties. Electron-deficient organic derivatives for electron-transfer media are inherently hard to come by. Conversely, nitration provides some of the easiest means for generating electron deficient conjugates and for bathochromically shifting their optical spectra. Concurrently, long singlet-exceed lifetimes of photo sensitizers ensure that the absorbed light energy can do some work, i.e., drive chemical conversions or generate electricity. Unfortunately, nitro groups tend to provide efficient pathways for non-radiative deactivation placing a stigma on fluorescent nitro-compounds. As unusual as it may sound, however, nitro-compounds can fluoresce. We focus on modulating the relative positions of the energy levels of the signet and triplet excited states to supress intersystem crossing (ISC) in nitropyrenes. Indeed, ISC is a principal pathway for deactivation of the singlet excited states of nitrated polycyclic aromatic hydrocarbons. Introducing some charge-transfer (CT) character to the singlet excited states, brings them slightly below the upper triplet states and supresses ISC. Introducing too much CT character, however, lowers the singlet excited states further, making the back charge transfer a dominant pathway for non-radiative decay, thus, lowering significantly the emission quantum yields. While we focus on nitropyrene, we can employ these principles for other nitrated polycyclic aromatic hydrocarbons. Considering the vibrational modulation of the CT dynamics provides an alternative means for controlling the excites-state kinetics of chromophores, which we have demonstrated with donor-modified diketopyrrolopyrroles. Understanding the balance between different pathways of deactivation of singlet excited states sets new design principles for electron-deficient chromophores and allows for removing the stigma around fluorescent nitro-compounds.

Tuesday 12th, 12:10-12:30

Non-RRKM Dynamics, Excited-State Aromaticity, and Regioselectivity on the Mechanism of the Triplet Di-π-Methane Rearrangement

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Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA [2]
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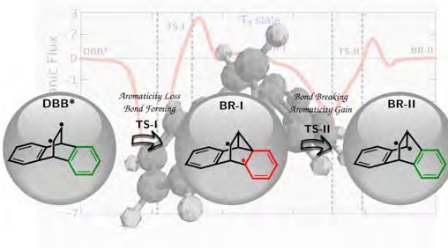
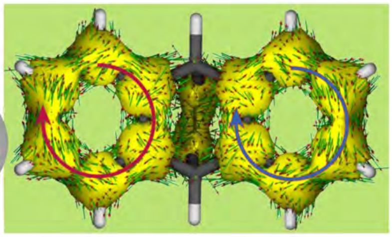
The photochemistry of the di-π-methane rearrangement has been studied by means of computational methods using both high-level and DFT calculations. In acyclic molecules, the reaction via triplet state does not effectively compete with photoisomerization of a double bond, although the triplet rearrangement is preferred for bicyclic molecules such as dibenzobarrelene (DBB), which leads to dibenzosemibullvalene (SBV) as product [1]. Photoexcitation via singlet S_1 state leads to a different product, a dibenzocyclooctatetraene. Upon triplet sensitization, DBB* can form a 1,4-biradical intermediate (BR-I) that leads to a 1,3-biradical intermediate (BR-II). From BR-II, the intersystem crossing (ISC), leading to the ground state, gives the SBV product. Invoking the Salem's rules for ISC of biradicals, the perpendicular orientation between non-orbitals in BR-II suggests a relatively facile ISC mechanism. Hence, the first transition state (TS-I) on T_1 should be determining in the reaction rate, with ca. 4 kcal/mol above the barrier associated to the second transition state (TS-II). In the mechanism of this [π^2+σ^2] rearrangement, one-step and two-step pathways compete on the triplet surface [1], since BR-I may bypass in the passive of the alkene triplet to BR-II. With molecular dynamics [2], the non-statistical nature in the dynamics was confirmed due to quasi-classical trajectories involve sequential formation and cleavage of bonds in BR-I with lifetimes ranging from 13 to 1160 fs. Interestingly, substituent effects can destabilize the radical species on T_1 and eventually BR-II becomes the regioselectivity determining step [3]. In a very recent work, the reaction electronic flux (REF) method was used to assess the effect of aromaticity along the reaction coordinate [4,5]. The REF could discriminate between electronic flux in π- and σ-bonds, thus suggesting the key role of aromaticity in the reaction mechanism. Effects arising from triplet antiaromaticity alleviation and the Baird's rule were studied as well [4,5].





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Oral Presentation O3

Tuesday 12th, 15:00-15:20

Im memoriam Enrique San Román (1945-2019)

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Enrique San Román was the founder of the Photochemistry Group in the College of Exact and Natural Sciences of the Universidad de Buenos Aires, after the recovery of Democracy in Argentina in 1983. In the presentation we will remember his efforts to build the group, his technical, scientific, and teaching abilities, as well as his wonderful personal qualities. After struggling some years with cancer, he left us in July 2019. He guided several PhD thesis and initiated a successful research project on the photophysics and photochemistry of highly concentrated dyes in solid matrices. Enrique and his students and collaborators were main contributors to all ELAFOT meetings as well as to the IUPAC Symposia on Photochemistry. Enrique, together with Fred Brouwer coordinated a large and ambitious IUPAC project on “Fluorescence Standards”.

Oral Presentation O4

Tuesday 12th, 15:20-15:40

Type I photosensitization of Ubiquitin leads to fluorescent adduct formation, cleavage and dimerization

Lara O. Reid,[1] Gabriela Petroselli,[2] Rosa Erra-Balsells,[2] Virginie Lhiaubet-Vallet,[3] Miguel A. Miranda,[3] Andrés H.Thomas,[1] M. Laura Dántola[1]

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Different compounds are able to induce photosensitivity as a result from exposure to certain molecules and light; these includes phototoxic and photoallergic reactions. The photoallergy normally involves a covalent binding between proteins and photosensitizer agents leading to the formation of a complete photoantigen, which may trigger a hypersensitivity reaction due to a cell-mediated immune response.

Pterins belong to a family of heterocyclic compounds present in a wide range of living systems and play different roles ranging from pigments to enzymatic cofactors for numerous redox and one-carbon transfer reactions. In pathological conditions, such as vitiligo, a skin disorder characterized by the acquired loss of constitutional pigmentation, pterins accumulate in the affected tissues at concentrations which are significantly higher than those reported for healthy cells.[1] Under UV-radiation, this compounds are able to photosensitize damage in proteins, DNA and their components by Type I (electron –transfer) and Type II (singlet oxygen) mechanisms.[1,2] Recently, it has been reported that, in the absence of molecular oxygen, pterin (Ptr) the parent and unsubstituted compound of oxidized pterins, is able to react with thymine (Thy) yielding an adduct Ptr-Thy in which the photosensitizer is covalently linked to the Thy moiety.[4]

Therefore, given the biological and medical relevance of the photosensitizing properties of pterins, the aim of this work is to study if Ptr is able to generate photoadducts with proteins and establish its photoallergic potencial. For this study, aqueous acidic solutions of Ubiquitin (Ub) and Ptr were irradiated (λ_{ex}=350 nm) at room temperature and in different atmospheres. Ub was used as a model protein given that is a small (8.5 kDa) regulatory protein, which has only one Tyrosine (Tyr) residue and none Tryptophan residue.The irradiated solutions were analyzed by UV/visible spectrophotometry, HPLC, fluorescence spectroscopy, SDS-PAGE and mass spectrometry (MALDI-TOF and nano LC-ESI-Orbitrap).

Under UV-A radiation Ptr is able to form an adduct with Ub, and this reaction is much more efficient in the absence of O_2. The spectroscopic analysis reveals that the emission and the excitation spectrum are similar to those corresponding to Ptr, as well as the fluorescence lifetime. On the other hand, as a consequence of the photosensitized process, the protein suffers oligomerization mediated by Tyr dimers, and also a fragmentation can occur, which is dependent of the oxygen concentration in the atmosphere.

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Oral Presentation O5

Tuesday 12th, 16:50-17:10

Antioxidant action of Resveratrol in the prevention of guanine photosensitized oxidation

Jael R. Neyra Recky, Maira Gaspar Tosato, Mariana Paula Serrano, Andrés H. Thomas and M. Laura Dántola, Carolina Lorente

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), CCT La Plata-CONICET. Diagonal 113 y 64, (1900) La Plata, Argentina

Resveratrol (3,4´,5,-trihydroxystilbene, RSV) is a natural polyphenolic compound naturally present in a variety of plant species, especially in fruits and flowers such as grapevines, nuts, lilly flowers, and it is synthesized in response to stress situations such as infections or UV radiation.[1,2] During the last years, the interest in RSV has increased due to the evidences found of many beneficial properties against aging and for the prevention and/or treatment of various diseases such as cancer, Alzheimer and cardiac dysfunction[3-6]It has been reported that pterin (Ptr), is able to photosensitize the degradation of the purine nucleotide 2'-deoxyguanosine 5'-monophosphate (dGMP) in aqueous solution.[7,8] In acidic conditions the main mechanism of this process is type I mechanism, and is initiated with an electron transfer from dGMP to triplet excited state of Ptr (^{3}Ptr*), where the guanine radical cation (dGMP$^{\bullet+}$) is formed (Scheme).[9] This radical undergoes fast deprotonation to form the neutral radical (dGMP(-H$^+$)$^\bullet$), which as previously described by Cadet *et al*, is the origin of oxidative damage on DNA molecules from one-electron oxidation by diverse chemical or physical oxidizing agents, and in aqueous media suffers nucleophilic addition or deprotonation reactions yielding several products.[10]

$$\mathrm{Ptr} \xrightarrow{h\nu} {}^1\mathrm{Ptr}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{Ptr}^* \qquad (1)$$

$${}^3\mathrm{Ptr}^* + \mathrm{dGMP} \longrightarrow \mathrm{Ptr}^{\bullet-} + \mathrm{dGMP}^{\bullet+} \qquad (2)$$

$$\mathrm{dGMP}^{\bullet+} \longrightarrow \mathrm{dGMP(-H)}^{\bullet} + \mathrm{H}^+ \qquad (3)$$

$$\mathrm{Ptr}^{\bullet-} + \mathrm{O_2} \longrightarrow \mathrm{Ptr} + \mathrm{O_2}^{\bullet-} \qquad (4)$$

$$2\,\mathrm{H}^+ + 2\,\mathrm{O_2}^{\bullet-} \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad (5)$$

$$\mathrm{dGMP(-H)}^{\bullet} \xrightarrow{\mathrm{O_2}^{\bullet-}/\,\mathrm{O_2}/\mathrm{H_2O}} \mathrm{dGMP(ox)} \qquad (6)$$

Kinetic analysis (HPLC-UV, UPLC-MS) during steady-state irradiation (λ_{IRR} = 365 nm)) indicates that RSV protects dGMP from oxidation. By fluorescence and laser flash photolysis experiments (LP980, Edinburgh) the bimolecular quenching rate constants of ^{1}Ptr*, ^{3}Ptr* and dGMP(-H$^+$)$^\bullet$ with RSV were determined (1.1(±0.1)x10^{10}s^{-1}M^{-1}, 4.94x10^9 M^{-1}s^{-1} and 1.2x10^9 M^{-1}s^{-1}, respectively).[10] Taking into account the rate constants and the lifetimes values of the involved species (^{1}Ptr* (7.8 ns), ^{3}Ptr* (~6 μs), dGMP(-H)$^\bullet$ (>100 μs)), at low concentration of RSV, the antioxidant reacts significantly only with dGMP(-H)$^\bullet$, recovering the nucleotide and preventing its further oxidation. The results presented in the current study clearly demonstrate that RSV is efficient in the protection of dGMP from one-electron oxidation.

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Wednesday 13th, 10:10-10:30

A Cyrhetrenyl Acylhydrazone Photoswitch: Synthesis, Characterization and Singlet Oxygen Generation.

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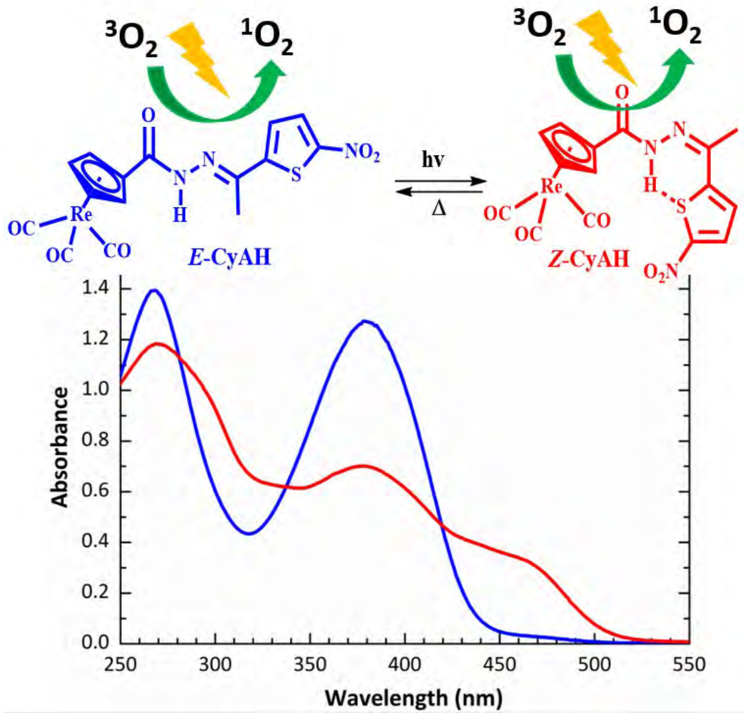
A novel cyrhetrenyl acylhydrazone of formula $[(\eta^5\text{-}C_5H_4)\text{-}C(O)\text{-}NHN{=}C(CH_3)\text{-}(2\text{-}C_4H_2S\text{-}5\text{-}NO_2)Re(CO)_3]$ (**CyAH**) has been synthesized. This complex was full characterized by FT-IR spectroscopy, mass spectrometry, ^{1}H NMR, and structural X-ray diffraction. Their photophysical properties were investigated using steady state and time-resolved emission spectroscopy. The crystal structure reveals that **CyAH** adopts the *E*-configuration around the iminic bond [-N=C(CH$_3$)]. The electronic absorption spectrum of ***E*-CyAH** displays a band at 380 nm with $d_\pi \rightarrow \pi^*$ metal to ligand charge transfer (MLCT) character, which is consistent with TD-DFT theoretical results. Under 365 nm light irradiation, ***E*-CyAH** shows photoisomerization *E*/*Z* and thermal back isomerization processes, which were investigated through UV-Vis and ^{1}H-NMR spectroscopies. We found that the ***Z*-CyAH** isomer is formed due to stabilization through an intramolecular H-bond between the N-H of the hydrazone group and the sulfur atom from 5-nitro-2-thiophenyl moiety. In addition, both **CyAH** isomers are efficiently able to photosensitize the generation of singlet oxygen ($^1O_2$ ($^1\Delta_g$)) with good yield ($\Phi_\Delta = 0.342$). These results demonstrate that the incorporation of the $[Re(\eta^5\text{-}C_5H_4)(CO)_3]$ core bonded to a photo switchable fragment makes it a new type of organometallic photoswitch and photosensitizer for singlet oxygen generation.



Wednesday 13th, 12:10-12:30

Ruthenium-functionalized Silica as Heterogeneous Photocatalysts

Rodolfo I. Teixeira, **Simon J. Garden**$^{\delta}$ **and Nanci C. de Lucas***

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Photocatalysis has become a prominent theme in organic chemistry as a unique and effective tool for electron or energy transfer processes under mild reaction conditions.[1] Ruthenium(II) complexes have demonstrated useful properties as photocatalysts.[2] Although ruthenium complexes have been extensively studied as photocatalysts in homogeneous medium, a few examples of heterogeneous photocatalysts based on ruthenium have been investigated. Thus, we explore the modification of silica with ruthenium complexes and the use of these materials for photocatalysis.

The ruthenium complexes $[Ru(bpy_2)dppa](PF_6)_2$ and $[Ru(phen)_2dppa](PF_6)_2$ (where bpy = 2,2'-bipyridyl, phen=1,10-phenanthroline and dppa=dipyrido[3,2-a:2',3'- c]phenazine-11-carboxylic acid) were prepared and attached to the APTES-modified surface silica surface by using DCC as the coupling agent. The materials were characterized by diffuse reflectance (DR), emission spectroscopy, XPS and ICP-OES. DR experiments revealed absorption in the region of 400 nm to 500 nm (λ = 450 nm) and emission in the region of 500 nm to 700 nm (λ_{em} = 590 nm), characteristic of ruthenium complexes. XPS analysis exhibited the presence of Ru(II) with a binding energy of 280.3 eV characteristic of the Ru ($3d_{5/2}$).[3] The ruthenium on the silicas was quantified by ICP-OES to be 150 ppm for $[Ru(bpy_2)dppa](PF_6)_2$ and 170 ppm $[Ru(phen)_2dppa](PF_6)_2$.

In order to investigate the photocatalytic activity of the developed materials, the [2+2]-cycloaddition of 3-(2-oxo-2-phenylethylidene)-2-oxindole and the coupling between *N*,*N*-dimethylaniline and *N*-phenylmaleimides were investigated. For the [2+2]-cycloaddition of 3-(2-oxo-2-phenylethylidene)-2-oxindole a MeOH (10 mL, 100 mM) solution was irradiated with the modified silica (10 mg) and full conversion was observed within 6h when irradiating with a 100W blue LED (460-463 nm). For the coupling reaction, a mixture of *N*,*N*-dimethylaniline (0.5 mmol) with *N*-phenylmaleimide (0.25 mmol) was irradiated with the modified silica (10 mg) in DMF (10 mL) and a conversion of 80% was observed within 6h of irradiation. Irradiation experiments in the absence of catalysts, or experiments in the presence of catalysts but without irradiation, were performed and no considerable conversion of the reactants was observed.

The energy transfer mechanism was investigated by Stern-Volmer quenching experiments of the emission at 620 nm and of triplet absorption at 370 nm of the ruthenium complexes in solution. A quenching constant of $6\text{-}7 \times 10^{9}$ L mol^{-1} s^{-1} for the 3-(2-oxo-2- phenylethylidene)-2-oxindole indicating that the reactant can effectively participate in the photocatalytic cycle of the ruthenium catalyst. *N*,*N*-dimethylaniline revealed a quenching constant of $1\text{-}2 \times 10^{9}$ L mol^{-1}s^{-1} and *N*-phenylmaleimide exhibited a quenching constant 0.7- 1×10^{8} L mol^{-1} s^{-1}. These results suggest that the *N*,*N*-dimethylaniline is the reactant involved in the catalytic cycle with the ruthenium complexes.

In conclusion, these materials are an interesting alternative as photocatalysts for expanding the scope of ruthenium-based photoredox reactions in heterogeneous media.

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Wednesday 13th, 15:40-16:00

Sunscreen-Based Photocages for Topical Drugs

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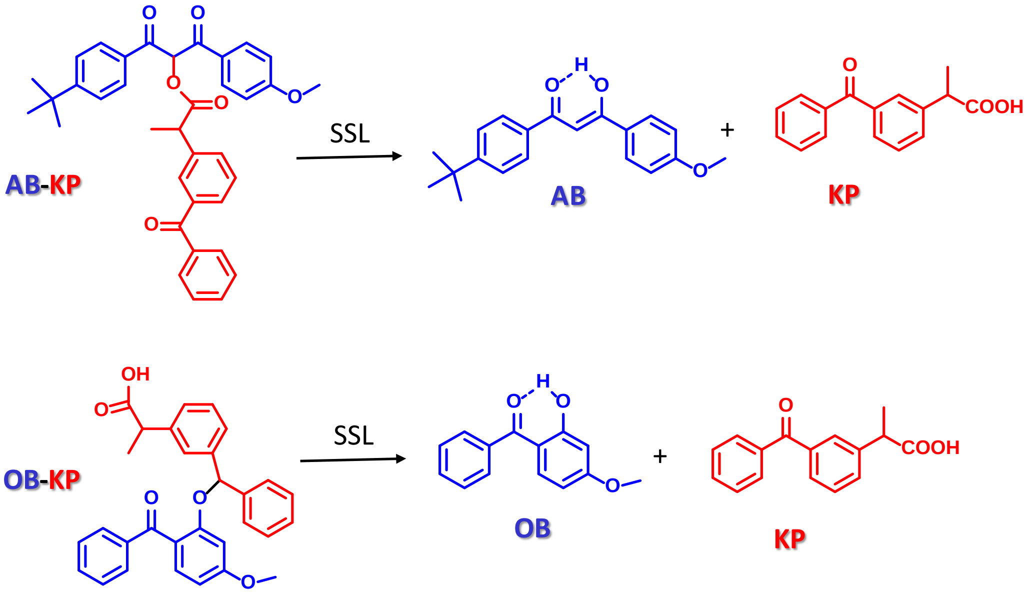
Topical drugs generally show a better safety profile than their systemic counterparts. Nonetheless, they are not always innocuous and present drawbacks mainly associated with their interaction with solar radiation. In this context, the non-steroidal anti-inflammatory agent ketoprofen (KP) is one of the most representative examples of photosensitive drugs due to its extensive use in daily life by outdoor workers or sportsmen.[1]



Phototriggered release of ketoprofen (KP) and its protecting shield AB or OB.

Here, a sunscreen-based photocage (ie. a covalently linked pro-drug/pro-filter system) has been developed to overcome KP photoreactivity, and to allow controlled and simultaneous photorelease of the masked drug and the solar filter.[2] The concept has been proved using two well-established solar filter avobenzone (AB) and oxybenzone (OB).

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Oral Presentation O9

Thursday 14th, 9:40-10:00

Dihydrodioxin Photochemistry as a Tool in DNA Cleavage

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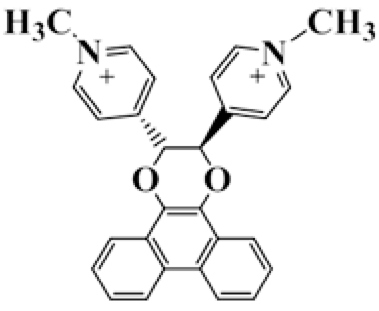
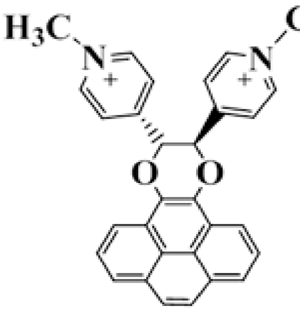
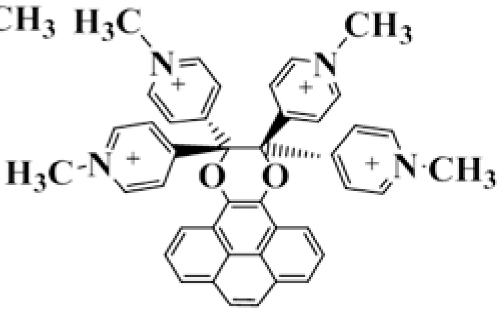
The photochemistry ans DNA cleaving properties of the following dihydrodioxins I,II and III and related materials will be described.



I



II



III

SHORT

TALKS

Abstracts

Short Talk S1

Wednesday 13th, 16:30-16:45

New approach on Tyrosine photosensitized oxidation mechanism

Jael R. Neyra Recky, Mariana P. Serrano, Andrés H. Thomas, M. Laura Dántola, Carolina Lorente

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Pterins are a family of heterocyclic compounds widespread in biological systems playing different functions. Under UV-A radiation (320–400 nm), these molecules can act as photosensitizers through both type I and type II mechanisms.[1,2] Pterin (Ptr), the parent unsubstituted compound of oxidized pterins, is able to oxidized tyrosine (Tyr)[3] under UV-A radiation. The mechanism is initiated by an electron transfer reaction from Tyr to Ptr triplet excited state (^{3}Ptr*) to yield the Ptr radical anion ($\text{Ptr}^{\bullet-}$) and tyrosine radical cation ($\text{Tyr}^{\bullet+}$) (reaction 1). The $\text{Tyr}^{\bullet+}$ may deprotonate to generate tyrosyl radical ($\text{Tyr(-H)}^{\bullet}$) (reaction 2). In the presence of O_2, electron transfer from $\text{Ptr}^{\bullet-}$ to O_2 regenerates Ptr producing $O_2^{\bullet-}$ (reaction 3). The $O_2^{\bullet-}$ may disproportionate to form H_2O_2 (reaction 4). Finally, a group of processes represented by reaction 5 led to Tyr oxidation. Alternatively, radical dimerization might contribute to Tyr consumption (reaction 6). Tyrosine dimers (Tyr_2), 3,4-dihydroxyphenylalanine (DOPA) and dopachrome were identified as photoproducts. The mechanism of Tyr_2 generation is well known. Nevertheless, in literature, there’s no consensus on the pathways that originate DOPA and dopachrome.

$$\begin{array}{lcll}
{}^3\text{Ptr}^* + \text{Tyr} & \longrightarrow & \text{Ptr}^{\bullet-} + \text{Tyr}^{\bullet+} & (1) \\
\text{Tyr}^{\bullet+} & \longrightarrow & \text{Tyr(-H)}^{\bullet} + \text{H}^{+} & (2) \\
\text{Ptr}^{\bullet-} + O_2 & \longrightarrow & \text{Ptr} + O_2^{\bullet-} & (3) \\
2O_2^{\bullet-} + 2\text{H}^{+} & \longrightarrow & H_2O_2 + O_2 & (4) \\
\text{Tyr(-H)}^{\bullet} + H_2O/O_2 & \longrightarrow & \text{Tyr}_{(\text{ox})} & (5) \\
2\ \text{Tyr(-H)}^{\bullet} & \longrightarrow & \text{Tyr}_2 & (6)
\end{array}$$

Simplified scheme of the photosensitization of Tyr by Ptr

The main goal of this work is to elucidate the pathways involved in the photogeneration of DOPA and dopachrome, by evaluating the role of reactive oxygen species (ROS) and $\text{Tyr(-H)}^{\bullet}$. Acid aqueous solutions (pH 6.0) containing Ptr (60μM) and Tyr (100μM) were exposed to UV-A radiation (365 nm) for different periods of time and in different experimental conditions: *(i)* in the presence of superoxide dismutase (SOD) (0 – 50 U/mL), to evaluate the role of $O_2^{\bullet-}$; *(ii)* in D_2O to evaluate the role of $^1O_2$; and *(iii)* in presence of resveratrol (RSV), a natural antioxidant inhibitor of type I photooxidation mechanism, to evaluate the role of ($\text{Tyr(-H)}^{\bullet}$).[4]

The results obtained using different experimental conditions suggest that the main products previously reported (Tyr_2, DOPA and dopachrome) are generated from $\text{Tyr(-H)}^{\bullet}$. The experiments perfomed in the presence of SOD, confirmed that DOPA is a product of the reaction between $\text{Tyr(-H)}^{\bullet}$ and $O_2^{\bullet-}$. On the other hand, the contribution of $^1O_2$ to the formation of these oxidation products may be discarded.

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Wednesday 13th, 16:45-17:00

Characterization and membrane affinity of decyl-lumazines

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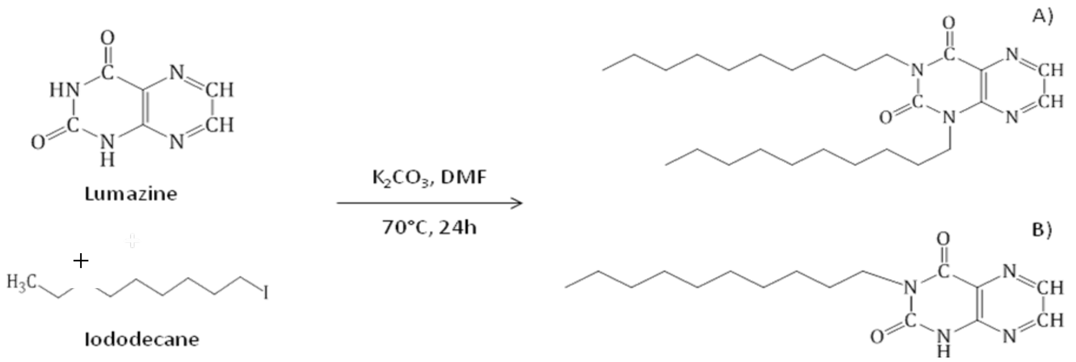
Pteridines are a family of heterocyclic compounds, which are present in biological systems and play different roles ranging from pigments to enzymatic cofactors for numerous redox[1]. Within the pteridine family, pterins are those compounds derived from 2-aminopteridine-4(3H)-one (pterin, Ptr) and lumazines are those derived from pteridine-2,4(1,3H)-dione (lumazine, Lum). Lumazine derivatives are present in cells, since 6,7-dimethyl-8-ribityllumazine is the biosynthetic precursor of riboflavin (vitamin B2), and also as the main degradation products from the metabolic degradation of all reduced pterins.

Under UVA radiation (320-400 nm) lumazines can fluoresce, undergo photooxidation to produce different photoproducts and generate reactive oxygen species. They can also act as photosensitizers on biomolecules such as nucleotides and DNA[2].

The aim of this work was the synthesis and characterization of new alkylated lumazine derivatives, that could act as fluorescent probes in biomembranes. To synthesize the compounds, a nucleophilic substitution (SN2) reaction was used. After the purification, two compounds were obtained: compound A (lumazine + 2 decyl chains) and compound B (lumazine + 1 decyl chain). These new lumazine derivatives were characterized by NMR mono and two-dimensional (^{1}H, ^{13}C, HSQC, HMBC). In addition, they were identified using High Performance Liquid Chromatography (HPLC), Thin Layer Chromatography (TLC) and UV-visible Spectrophotometry. Also spectroscopic properties were studied, getting absorption and emission spectra and fluorescence quantum yields.

In addition, the interaction of these compounds with biomembranes was studied, using large unilamellar vesicles (LUVs) as a biomimetic model, determining the binding constants and its ability to photoinduce oxidation of phospholipids.



Scheme 1. Synthesis reaction for the obtaining of compounds A) 1,3-didecylpteridine-2,4(1H, 3H)-dione and B) 3-decylpteridine-2,4(1H,3H)-dione.

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Thursday 14th, 10:00-10:15

Study of spectroscopy properties of carbon nitride quantum dots

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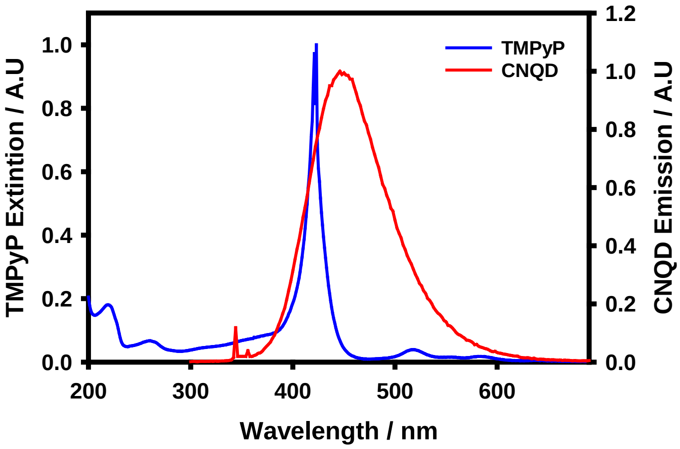
Carbon nitride quantum dots (CNQD) are in constant development and study. Features as good conductivity, high chemical stability, low toxicity, strong photoluminescence and interesting optical properties, make them appropriate for a wide range of applications [1]. The aims of this work are: i) to evaluate the generation of reactive oxygen species (ROS) upon irradiation of suspensions of CNQD prepared by different methods and ii) to investigate the effect of CNQD on the ROS generation by organic photosensitizers.

CNQD can be synthesized by low temperature routes, which are in continuous development with excellent results [2,3]. Here, we prepare CNQD by five different methods employing different precursors at low temperature and we characterize them by a battery of physico-chemical methods. The generation of singlet molecular oxygen was evaluated by time-resolved phosphorescence at 1270 nm and the production of hydrogen peroxide was determined by a colorimetric assay.

The photoluminescence of the CNQD, as well as their interaction with 5,10,15,20-Tetrakis (1-methyl-4-pyridinio) porphyrin tetra(p-toluenesulfonate) (TMPyP), was studied by steady-state emission spectroscopy. Because the fluorescence spectrum of the CNQD overlapps the absorption spectrum of TMPyP, a possible energy transfer mechanism was considered.



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POSTERS

Abstracts

Poster Po1

Rational Design of bicarbazoles for the construction of Organic Light-Emitting Diodes (OLEDs)

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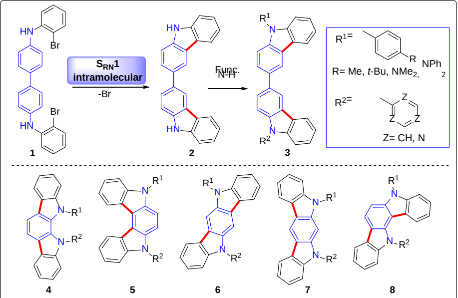
Carbazoles and bicarbazoles (such as **3**) are interesting synthetic molecules as they play important roles in the construction of Organic Light-Emitting Diodes (OLEDs).[1] In this work, we propose the synthesis of different families of bicarbazoles (e.g.: **2**) by photoestimulated Unimolecular Radical-nucleophilic Substitution ($S_{RN}1$) under mild conditions as absence of metal compounds, visible light and room temperature, using the corresponding diarylamines (**1**) as substrates (Scheme 1). Once the bicarbazoles are obtained, they will be functionalized with electron-donor groups (R^1) and electron-withdrawing groups (R^2).

In order to be suitable for the construction of OLEDs, the organic molecules must gather certain characteristics: high photoluminescence quantum yield (PLQYs), small Singlet- Triplet Energy gap ($\Delta E_{S\text{-}T}$), low molecular flexibility, among others. These properties have a direct impact in the efficiency of the device. Besides, since we are interested in blue OLEDs, the emission fluorescence band should be at approximately 460 nm.

In the first place, to avoid the tedious synthesis of a set of molecules, which involves many steps, molecular modeling studies were carried out to choose the better candidates for the construction of the device, taking into account the characteristics mentioned above. We arranged in six groups the different compounds, based on the nucleus of the carbazole or bicarbazole (**3**-**8**) and a suitable acceptor (R^2), taking into account all the possible combinations. As a first approximation, we calculated HOMO-LUMO energy difference in the ground state, using DFT and $\Delta E_{S\text{-}T}$ using TD-DFT. To obtain high PLQYs, it is suggested that the values of these two energies should be small enough (<0.3 eV) in order to achieve thermally activated delayed fluorescence.[2]

Here, we present the results of the synthesis of the bicarbazoles (from the respective diarylamines) which exhibited the best molecular properties as suggested by DFT and TD-DFT calculations.



Scheme 1. Bicarbazoles for construction OLEDs

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Poster Po2

Metal atom effect on the photophysical/photochemical properties of curcumin derivatives

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Curcumin is a natural yellow pigment isolated from rhizomes of Curcuma longa, extensively used in India for centuries as a spice and medicinal agent. Curcumin exhibits antioxidant and anti-inflammatory activities, and has recently been recognized as photosensitizer (PS) for application in photodynamic therapy (PDT) due to the generation of reactive oxygen species (ROS), showing antimicrobial, antifungal and antitumoral activities[1]. However, the practical use of curcumin as PS is limited, because its poor bioavailability, easily photodegradability and low quantum yield of singlet oxygen ($\Phi_{\Delta MeCN} = 0.11$)[2].

Curcumin derivatives possess two α, β unsaturated carbonyl groups that exist in a stable enol form which can be used as chelating ligands toward a variety of metals and to form stable complexes. Binding curcumin to a metal ion significantly reduces the tendency of this PS to undergo hydrolysis in aqueous medium and hence resulting in improved bioavailability and therapeutic efficacy[3]. Besides, the metal complexation can improve the quantum yield singlet oxygen generation, once chelation of metals increase the intersystem crossing (ISC) due to heavy atom effect[4].

In this work, we studied the heavy atom effect on the photophysical/photochemical properties by metal chelation in curcumin moiety (Figure 1-a). The synthesis of the new metal complexes of curcumin derivatives using diamagnetic metals Zn (II) and Pd (II), was successfully performed by starting from 1,10-phenanthrolin bidentate ligand (Figure 1-b). The improve of quantum yield of singlet oxygen generation was observed after the metal complexation in relation to free molecule (Table 1). Further, the fluorescence quantum yield decreased, as expected, due to the heavy atom effect and the most pronounced one can be observed for Pd (II) complex. Also, excited state deactivation is reduced due to a minimization of degrees of freedom after metal chelation which contributes to singlet oxygen formation[4,5]. The results shown that metal complexes of curcumin derivatives (2) an (3) are promising candidates to PDT application.

Table 1: Photophysical and photochemical properties.

Comp.	**Log ε**	**Φ_{flu}**	**Φ_{Δ}**	**τ(ns)**	**τ_T(μs)**	**τ(ns)***
1	4.90	0.33	0.31	1.56	4.91	1.61
2	4.79	0.30	0.40	1.53	8.75	1.84
3	4.99	0.29	0.55	1.55	13.05	1.79

Solvent: CH_2Cl_2 λ_{exc} = 497 nm λ_{em} = 590 nm *solid state

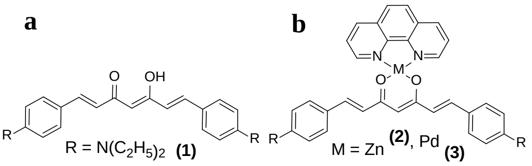

Figure 1: Curcumin derivative structures.

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Poster Po3

Solvent polarity effect and dual fluorescence behavior of a novel chalcone derivative

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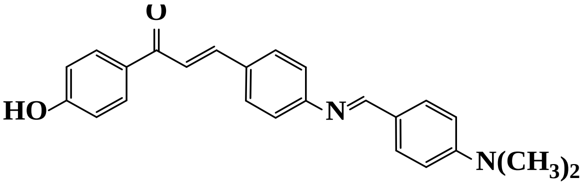
Chalcones are molecules with structures consisting of two aromatic rings linked by an α,β-conjugated keto-enol group. Several chalcone derivatives have been reported to be used as sensing materials for chemical sensors and as dyes for new optically active materials, among other applications. Due to this peculiar structure, chalcone and its derivatives are able to present some interesting features, like internal charge transfer (ICT) mechanism in the excited state. As a contribution in this field and further investigation of the photophysics of this molecular group, a new chalcone derivative was synthesized and its electronic behavior in the presence of different solvents was assessed. The new chalcone was synthesized by reacting a precursor chalcone with a *p*-substituted benzaldehyde. The resulting compound was the *p*-substituted iminochalcone (**ICh**).



3-(4-((4-(dimethylamino)benzylidene)amino)phenyl)-1-(4-hydroxyphenyl) prop-2-en-1-one

Electronic absorption spectra of **ICh** were determined in solvents of different polarities (Fig.1). A bathochromic shift of the maximum can be observed when increasing the solvent polarity (EtOAc < MeCN). This effect is more evident in MeOH, due to the protic nature of the solvent that stabilizes more efficiently the chalcone dipolar structure of the ICT excited state. The fluorescence spectra are also affected by the solvent properties. Whereas in MeCN, **ICh** displays a dual fluorescence behavior, in MeOH this effect is not observed (Fig. 2). In MeCN, the fluorescence band at higher energy arises from a typical ICT state, whereas the second band derives from the state known as twisted-ICT. Furthermore, the hypsochromic shift observed in MeOH, is probably caused by the protonation of the $-N(CH_3)_2$ group, that decreases the delocalization in the ICT state, increasing the emission energy process.

Fig. 1. Absorption spectra of **2a** (2×10^{-5} M) in MeOH (—), MeCN (—) and EtOAc (—)

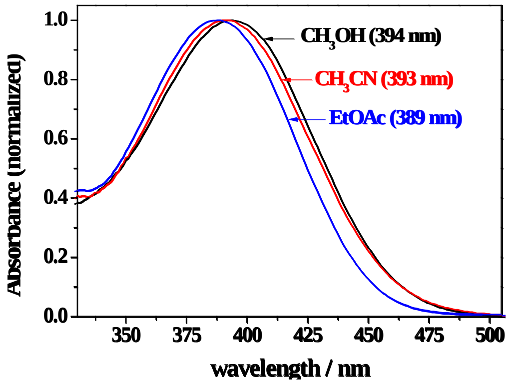
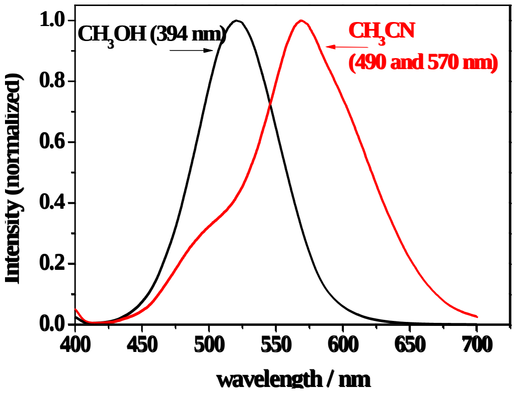


Fig. 2. Emission spectra of **2a** (2×10^{-5} M) in MeOH (—) and MeCN (—). λ_{ex} = 390 nm.



Fruit, Flower and Wine Inspired Fluorescent Chromophores

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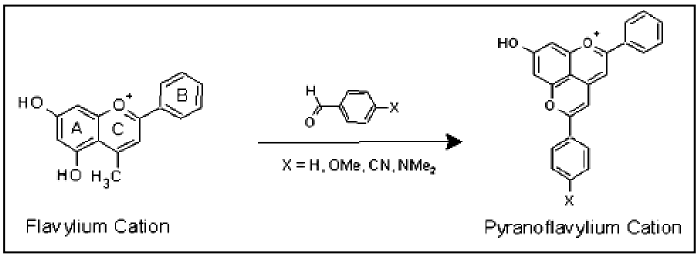
The colors of anthocyanins, the natural plant pigments responsible for most of the red, purple and blue colors of flowers, fruits and leaves, are modulated by pH, substitution and complexation with metal ions and/or colorless organic molecules (copigments) [1]. Anthocyanins (and analogous synthetic flavylium cations) are very efficient at absorbing and dissipating light energy, which enhances their photostability but makes them less interesting as chromophores in practical applications. During the maturation of red wine, the anthocyanins of grapes are transformed into pyranoanthocyanins, which have a pyranoflavylium cation chromophore [1]. The relatively facile synthesis of substituted pyranoflavylium cations permits manipulation of the redox properties and the nature of the lowest excited state (TICT, charge-transfer or localized) [2]. This excited state character, together with absorption spectra and excited state energies, can be nicely reproduced by *ab initio* quantum chemical calculations (ADC(2) combined with COSMO simulation of solvent environments), facilitating the rationalization of the observed photophysical behavior and the design of new falvylium and pyranoflavylium cation derivatives.



Unlike the natural pigments, synthetic flavylium and pyranoflavylium cations can be quite fluorescent. In contrast to anthocyanins and flavylium cations, pyranoflavylium cations form long-lived triplet states and singlet oxygen [3], and show reversible redox behavior and large two-photon absorption cross sections [4]. By circumventing the ultrafast energy dissipation pathways that contribute to the photostability of their natural pigment analogs, synthetic pyranoflavylium cations serve as a convenient chromophoric moiety for the rational design of fluorescent pigments [5], novel PDT sensitizers [4] and photoredox catalysts.

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Poster Po5

Characterization of magnetic photocatalyst with environmental applications

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Heterogeneous photocatalysis has rapidly emerged as the most attractive AOP (Advanced Oxidation Processes) in recent years for the destruction of organic, inorganic, and microbial pollutants due to a number of advantages, such as its versatile nature in terms of the variety of pollutants that can be removed, the potential to completely mineralize organic pollutants, the ability to use solar radiation in some cases to reduce the operational costs, and its capacity of being reused in several treatment cycles.[1] However, some limitations regarding recovery and reuse of the photocatalysts have inhibited their application in real systems. This issue can be overcome providing magnetic properties to the photocatalysts allowing an efficient separation and recovery with an external magnetic field. In this work, magnetic nanocomposites were developed to be used as photocatalysts in photochemical treatments for the degradation of pollutants from wastewater. Ag/Fe_3O_4 nanocomposites (NCs) were synthesized using starch as both a biocompatible capping agent for Fe_3O_4 nanoparticles and a reducing agent for the reduction of silver ions in an alkaline medium[2] and an one-pot method through the redox reaction between Ag_2O and $Fe(OH)_2$ in absence of additional reductant.[3]

The NCs were thoroughly characterize by Fourier transform infrared spectroscopy (FT-IR), UV-Vis diffuse reflectance spectroscopy (DRS) and Laser flash-photolysis (LFP) experiments for Transient Absorption Spectroscopy. The capacity of the as-prepared NCs for the generation of reactive species under UVA light was evaluated by laser flash photolysis (LFP) experiments.

FT-IR spectra showed interaction between Fe_3O_4-starch and Fe_3O_4-PVP nanoparticles, organic functional groups from starch and bands assigned of the Fe-O, C-O, C-H and O-H bonds. The diffuse reflectance spectra (DRS) of the Ag-Fe_3O_4 nanomaterials evidenced a similarity between them, but different from that expected for a semiconductor material. Instead of an increase in reflectance in the region of higher wavelengths of the spectrum, they all have a wide band centered around 230 nm, a smaller one centered at 330 nm, and then, the intensity of the reflectance decreases homogeneously 400 to 800 nm. LFP showed the characteristic broad absorption assigned to the electron-hole pair.

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Novel Bifunctional Crosslinkers / Co-initiators Systems for Vinyl Photopolymerization Based on Silsesquioxanes and Riboflavin

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The development of new aqueous soluble crosslinkers and ecofriendly co-initiators with applications in photopolymerization represent a challenge in the improvement of new materials. However, the use of amines, as co-initiators of photopolymerization, difficult its application in the area of biomaterials. On the other hand, the scarce of water soluble crosslinkers also limit their use, above all in the synthesis of hydrogels and other materials synthesis in aqueous media.

In this work, four different functionalized silsesquioxanes (SSOF) are synthesized as novel water soluble crosslinkers containing amines groups in their structures (Figure 1). The developed materials consist of hybrid compounds based on SSOF, functionalized with methacrylate and amine groups. These characteristics allowed using them as co-initiators in aqueous photopolymerization, besides than crosslinkers. In these bifunctional materials, the co-initiators amine groups, inevitably remain attached to the polymer chain, due to crosslinkers reactions. These avoid the undesired effects due to the presence of free amines in the final material. The hybrid nature of the silsesquioxanes came from the Si-O-Si bonds that confer interesting properties such as thermal and chemical resistance, increase in stability, and possibility of functionalization, among others.

SSOF were characterized by FTIR, MALDI-TOF MS, ^{29}Si-NMR and ^{1}H-NMR coupled to Si. The efficacy as co-initiators in photopolymerization was evaluated following the kinetic of conversion of C=C of monomers against irradiation time, employing Riboflavin (B2 vitamin) as sensitizer (Figure 2). The bifunctional SSOF synthesized co-initiators present different polymerization rate that could be applied to control the structure and properties of the developed gels. Moreover, the polymerization rate of the photoinitiators systems Rf/SSOF show to be higher than the reference photoinitiation system Rf/TEOHA (see Figure 2).

Finally the cross linkers / co-initiators developed here were employed for the synthesized of hydrogels that were evaluated measuring their swelling capacity at different pHs. As expected, hydrogels display different properties according to the SSOF employed in the synthesis.

Figure 1. Chemical structures of SSOF.

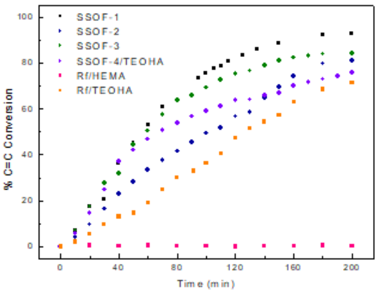

Figure 2. HEMA conversion % as a function of irradiation time for the polymerization initiated by different photoinitiation systems.

Photochemistry in Polyfunctional Steroids: Photorearrangement vs. Photoepimerization. Preparative and Mechanistic Studies

Matías I. Quindt[1], **Gabriel F. Gola**[2], **Javier A. Ramírez**[2] **and Sergio M. Bonesi**[1]

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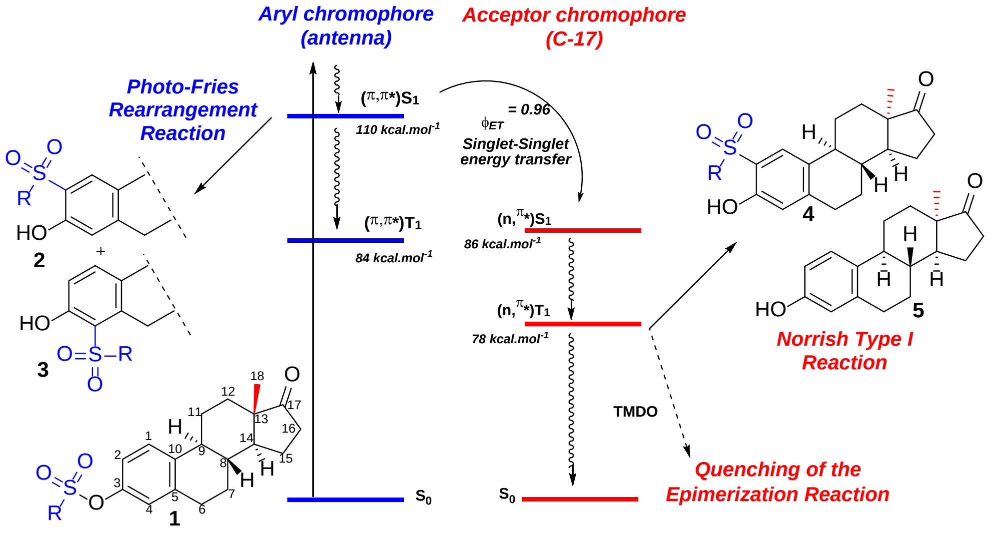
Recently, we have studied the photochemistry of some 3-acyl estrone[1] and as part of our ongoing research program we decided to study the photochemical behavior of some 3-arylsulfonyl- and 3-alkylsulfonyl estrone derivatives. Thus, direct irradiation of 3-sulfonylestrone **1** (see Scheme) with 254 nm in different solvents and under inert atmosphere (Ar) was carried out by means of steady-state conditions. Selective irradiation of the aryl chromophore of sulfonyl compounds underwent the photo-Fries rearrangement, with concomitant homolytic fragmentation of the sulfonic ester group and [1;3]-sulfonyl migration. This pathway afforded the *ortho*-sulfonyl estrone derivatives **2** and **3** as the main photoproducts. These steroidal photoproducts were obtained for the first time and were isolated by column chromatography and fully characterized by NMR spectroscopy.

On the other hand, estrone and the *ortho*-regioisomer **3** are found to epimerize upon irradiation with 254 nm light through a Norrish type I photoreaction. This reaction involves the triplet excited state of the carbonyl group (C-17) at the D ring of the steroids that is populated from the singlet excited state of the phenolic moiety through an intramolecular singlet-singlet energy transfer process with a high value of ϕ_{ET} (*ca.* 0.96)[2]. Photosensitization with acetone and chemical quenching with *N,N,N,N*-tetramethyldiazetinedioxide (TMDO) of the photo-Fries reaction confirmed that the photoreaction took place from the singlet excited state while Norrish type I reaction proceeds efficiently from the triplet excited state.

Solvent effects, as well as the nature of the sulfonyl group on the photoreactions, were also studied.



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Hantzsch Ester Anion as Electron Donor in Transition-Metal-Free Photoinducided *N*-Desulfonylation Reactions

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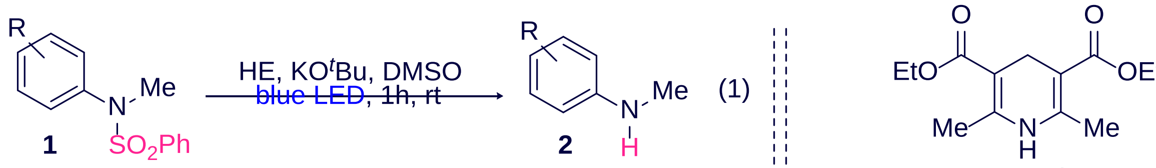
Hantzsch esters (HEs) have been used as reductants in catalytic hydrogenation reactions. Recently, with the advances in the visible light photoredox catalysis, it has been grown the use of HEs as electron donors and proton sources in many photoredox reaction types.[1] For example, in hydrodifluoroalkylation of alkenes,[2] reductive couplings of carbonyls with alkenes[3] or carboxylation of aromatic and aliphatic bromides and triflates.[4]

Sulfonyl group is useful for protecting nitrogen containing compounds. However, due to its great stability, requires rigorous deprotection conditions.[5] Recently, it has been developed a photocatalytic N-S cleavage using an iridium complex and the HE to give amides as products in excellent yields.[6]

Here, we report an efficient and transition-metal-free photoinducided desulfonylation method using the Hantzsch ester anion as promotor. The photostimulated reaction (visible light) of **1** (R=H), in the presence of HE anion (2 equiv.) in DMSO for 1 h afforded the deprotected product **2** (R=H) in 92 % yield at room temperature (eq 1). There was not reaction under dark conditions, which excludes a polar mechanism. The effect of the base was evaluated by carrying out the photostimulated reaction in the absence of KO^{t}Bu. Under this condition the product **2** was not obtained indicating that the base is necessary. Also, the reaction without HE only in presence of KO^{t}Bu (or NaH) gave the product in 15% yield. This result indicates that HE anion is responsible to initiate the ET reaction.



HE: Hantzsch ester

Our proposal is to investigate the mechanism of these visible-light-induced photo-removable sulfonyl group reactions supplying information from the study of experimental reaction conditions and photophysical properties.

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Poster Po9

Used Engine Lubricant Photodegradation in Seawater

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Spilled hydrocarbons from human sea-based activities are one important source of pollution in the ocean. Oily bilge wastewater from vessels can be discharged illegally into the sea or accidentally during routine operations, and generally includes lubricating oil, oily fluids, water and other wastes.

Used oil consists of aliphatic and aromatic hydrocarbons. Its composition is difficult to generalize because of additives degradation, contamination with combustion products or the presence of metals from the wear and tear of the engine [1].

The aim of this contribution is to evaluate the degradation by UV-A radiation of a used engine oil in seawater.

Fresh and used engine oil samples were collected from a fishing vessel at port. Seawater filtered through a 0.45 µm membrane filter was used. Seawater soluble fraction (SWSF) was obtained by adding used oil in seawater (1:10) after 24 hours of constant agitation employing a separatory funnel.

The SWSF was exposed to UV-A radiation for 15 hours. Dark controls were performed during the same period of time. Photodegradation was evaluated using UV-Vis absorption and emission spectroscopy. Fresh engine oil was used for calibration by means of total fluorescence spectra in conjunction with parallel factor analysis (PARAFAC). The amount of total petroleum hydrocarbons (TPH) was measured according to EPA 418.1 methodology [2].

Fluorescence and synchronous spectra of the used oil suggest the presence of aromatic compounds, like amine and phenol derivatives, usually used as additives [3] and polycyclic aromatic hydrocarbons. Absorbance and fluorescence intensity dropped after irradiation. The fluorescence spectra area is reduced around a 30 % after 15 hours.

Although lubricating oils are stabilized against photodeterioration by incorporating additives, the results obtained show that it can be partially degraded by UV-A radiation.

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Poster Po10

TiO_2 synthesis by the Pechini's method and application for diclofenac photodegradation

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In this work, the photodegradation of sodium diclofenac (DFNa) was evaluated using TiO_2 as catalyst synthesized via the Pechini method. The performance of the synthesized photocatalysts was compared with commercial Evonik® TiO_2 catalyst. The synthesis was performed according to the illustrated proposal (Figure 1), with adaptations to evaluate different calcination temperatures (500 to 700 ^{o}C) to obtain the oxide. In the experiments, the photodegradation of the DFNa was monitored spectrophotometrically (λ = 282 nm) and the toxicity of the photodegradation product evaluated with Artemia Salinas assays. The reaction conditions employed in the photodegradation were: 0.1 gL^{-1} TiO_2, 125 W Hg vapor lamp as irradiation source and pH of the reaction medium between 7.0 - 7.5. Photodegradation assays (Figure 2) showed a reduction of about 50% of the concentration of DFNa with 60 minutes of photodegradation. In the time range of 0 - 10 min the most significant concentration reduction values were estimated (Figure 3). The same performance also is shown for the apparent velocity constant (k_{app}) values that were estimated and presented in figure 4. Toxicity monitoring showed that the generated products had a reduction of up to 50% (Figure 5). The obtained results indicated that the synthesized TiO_2 samples had superior performance compared to Evonik® TiO_2.

Figure 1. TiO_2 synthesis

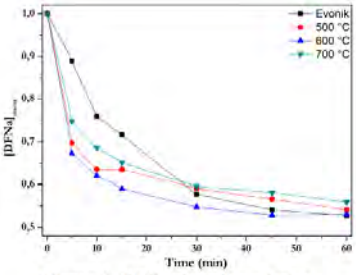

Figure 2. DFNa photodegradation

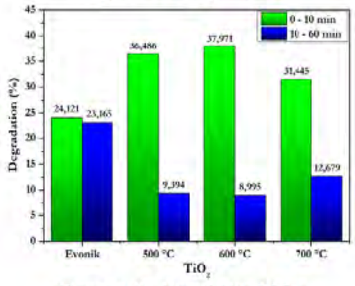

Figure 3. % degradation DFNa

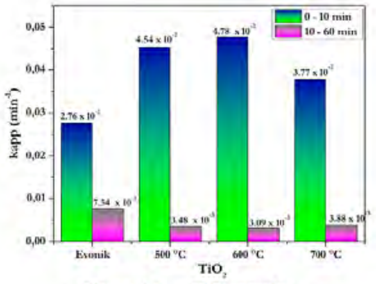

Figure 4. k_{app} TiO_2 samples

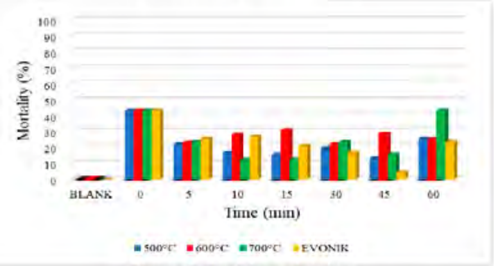

Figure 5. Toxicity reduction

Interaction and UV-A photodegradation study of graphene oxide with natural alkaloids

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Nowadays graphene oxide (GO) is among the most promising and functionalizable two-dimensional materials. Due to its high dispersability in water several researchers have explored the potential of GO for different biomedical and biotechnical applications. Chemically, GO has a fraction of carbon atoms with sp^3 hybridization and covalently bounded to oxygen functional groups (e.g., hydroxyl, epoxide and carbonyl groups) attached on the basal planes and edges of GO sheets. The remaining carbon atoms, with sp^2 hybridization, form clusters of various sizes, which mainly determine the optical and electronic properties of GO. It is a non-stoichiometric compound with a non-homogeneous structure and a very large specific area. It was recently reported that the planar structure and the π-conjugation of GO endowed it with excellent ability to immobilize a large number of substances, including metals, drugs, biomolecules and fluorescent molecules.

Since the analysis of the interaction between graphene oxide and small fluorescent molecules becomes important from a biotechnological viewpoint, we have investigated the behavior of GO suspensions in the presence of β-Carbolines (βCs). βCs are photoactive natural alkaloids present in a wide range of species, they derive from the structural unit 9H- pyrido[3,4-b]indole or *nor*harmane. Therefore, βCs are biocompatible compounds that also show several unique properties such as high chemical and photochemical stabilities. It is well known that the physicochemical behavior of βCs in aqueous environments is very varied given the presence of different substituents in the tricyclic system strongly affects their properties. In addition, upon UV-A excitation, βCs alkaloids are efficient photosensitizers, that can produce non-negligible quantities of singlet molecular oxygen ($^1O_2$), as well as other reactive oxygen species ($O_2^{\bullet-}$ and H_2O_2). Moreover, most of them also show high fluorescence quantum yields.

In this work we present a comparative study of the photodegradation of GO dispersions both in the presence and in the absence of βCs. Two GO samples, with different degree of natural oxidation, were used. In a first stage, interaction tests were carried out to characterize the molecular associations present in the mixtures. Subsequently, kinetic tests were carried out at pH 5.0, with stirring and under UV-A irradiation (λ_{irrad} = 368 ± 20 nm), both for the individual components, and for the mixtures of GO and βCs. The systems studied were monitored by UV-vis absorption and fluorescent excitation-emission spectroscopy. For the interpretation of spectroscopic results, multivariate analysis methods (MCR-ALS and PARAFAC) were applied in order to clarify the nature both of the interactions and of the photoinduced processes.

The results shows that GO have a strong electrostatic interaction with the βCs studied. Moreover, the presence of βCs produces a considerable decrease in the stability of the GO and the type of photoproducts obtained depends on the age of the starting GO.

Keywords: Graphene oxide, β-Carbolines, Interaction and UV-A photodegradation, Multivariate analysis.

Poster Po12

In Situ Photo Switching of Spirorhodamines Isomers in Solid State

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At present, the functional materials structurally switchable by stimuli such as heat, addition of cations, changes of pH, pressure, or light are the motive of innumerable studies to be ideal models to investigate the relation structure-function and new properties derived from that change. In this work we studied a family of spirorhodamines (SRAs), which are photochromic molecules with a switching mechanism based on the differences in the fundamental electronic state between isomers in solid state photochemical reaction.[1] It involves changes in the molecule structure and is thermally reversible.[2,3] In this work, assuming as hypothesis that in solid phase the permanence time in the optically active isomer is associated with its structural characteristics, a family of compounds modifying the substituent were synthetized.

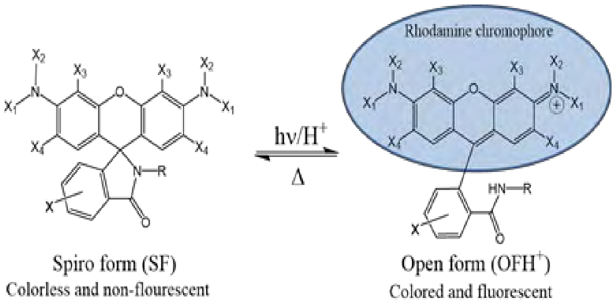

Fig. 1 General structure of spirorhodamines. The equilibrium responsible for the appearance of color is also shown. The forward reaction can be photo-induced with UV light, or by proton addition.

These equilibria were characterized in solid state by reflection, absorption and emission fluorescence spectroscopy, single crystal X-ray diffraction,[4] atomic force microscopy coupled to infrared spectroscopy[4] and computational calculations, evaluating the changes produced after irradiating the corresponding close isomer with ultraviolet light for each compound.

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Acknowledgments

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Synthesis, characterization and photophysical study of benzimidazol derivative as colorimetric and fluorimetric sensor for DMSO

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Simple analytical methods for aqueous DMSO samples in various concentration ranges are desirable for food or beverage quality control and environmental monitoring. However, such methods are limited because DMSO is highly hygroscopic, and its extraction from water is difficult.[1] Due to their diversity of applications and low toxicity,[2] the compound synthetized in this present work was mainly analyzed in this solvent to determine if they would be a solvatochromic sensor for this solvent.

We reported the synthesis of (*E*)-6-styryl-5,6-dihydrobenzo[4,5]imidazo[1,2-c]quinazoline **1** (Fig. 1) obtained by a condensation of 2-(2-aminophenyl)-1*H*-benzimidazole with cinnamaldehyde. The compound **1** was characterized by HRMS, FTIR, RMN (^{1}H, ^{13}C, 2D HSQC and DEPT-135). The solution of **1** in DMSO (10^{-5} mol L^{-1}) showed a greenish blue color under ambient-light and a green color under UV irradiation. In other solvents exhibited no color in ambient-light and a violet emission under UV irradiation. A bathochromic shift in the absorption spectra was observed as solvent polarity increases (Table 1). The steady state fluorescence spectra in DMSO showed two emission bands at 425 and 480 nm, while in other solvents was observed only one band at lower wavelengths. This led to an investigation of its structure in this solvent for future application of **1** as a selective sensor for DMSO. For further analysis about the structure, the time resolved emission spectrum of **1** in DMSO solution with temperature range from 25°C to 105°C was obtained. The results indicate the presence of a closed structure of **1** in the ground-state, in DMSO, and an equilibrium between the closed form and an opened form in the excited state occurring via a [1,5] sigmatropic-type shift.

Table 1. Photophysical and photochemical properties of **1** (10^{-5} mol L^{-1}).

	λ_{abs} (nm)	λ_{em} (nm)	Φ_f
DMSO	368	425 480	0.30^a (λ_{exc}=350nm)
Toluene	344	388 405	0.3^b (λ_{exc}=356nm)
THF	350	400	0.59^c (λ_{exc}=350nm)
MeOH	355	426	0.6^c (λ_{exc}=350nm)

Standards: a- Quinine sulfate in H_2SO_4 0.05M,
b- Anthracene in cyclohexane,
c- Benzo(a)pyrene in THF

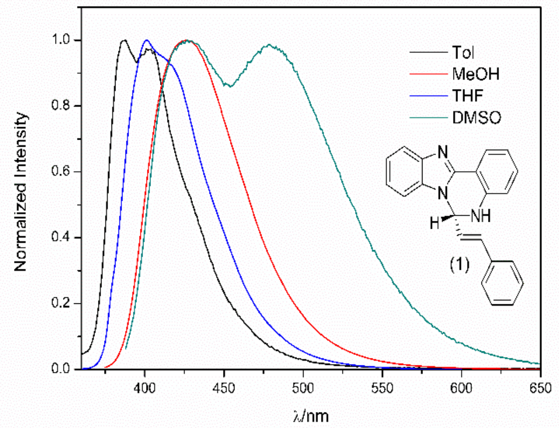

Fig. 1. Fluorescence spectra of **1** and its structure

Acknowledgments: CAPES and Chemistry Institute UFRJ

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11*H*-Pyrido[2,1-*b*]quinazolin-11-one - A reversible Turn-on/off Fluorescent Probe for Solution and Gas-phase Detection of Acids or Basic Amines

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Fluorescent sensors are important for the detection of many analytes due to lower detection limits, high sensitivity and selectivity, short response time and *in-situ* detection.[1,2] In this context, the monitoring of the acidity of a medium *in-situ* is important in the food industry, water treatment, biological processes, and the chemical industry.[3] Furthermore, detecting acid in the gas-phase, such as hydrochloric acid (HCl), acetic acid (AcOH) or trifluoroacetic acid (TFA) is of interest as a variety of processes can occur using gas-phase acids and these vapours can be dangerous. Thus, in the present study, we detail a metal- and solvent- free synthesis of *1H*-pyrido[2,1-*b*]quinazolin-11-one (**1**) and its photophysical properties as an acid or base sensitive sensor.

Compound **1** was prepared by heating 2-bromopyridine and methyl anthranilate (1.1 equiv.) in a screw-capped vial at 140 °C for 1 hour. The contents of the vial were extracted with EtOH and treated with aqueous K_2CO_3. The precipitate was collected and purified on a short column of silica to give the title compound as a yellow solid (65% yield). The absorption spectra, registered in organic solvents revealed a small blue shift on passing from a nonpolar to a polar solvent. However, when the absorption spectra were measured in buffered aqueous solution at pH 1, 7 and 14, the spectra revealed the presence of three distinct species with distinct pH dependent absorption spectra. Additionally, the emission spectra recorded in different organic solvents revealed only minor differences between the solvents, but on recording the emission spectra at different buffered pH's, a strong dependency on the pH was observed. At pH 14 no fluorescence was observed whilst at pH 7 the emission spectrum was essentially identical to that in acetonitrile but slightly blue-shifted whereas at pH 1 the emission intensity skyrocketed. Notably, the changes are reversible; acidification of the basic sample gave the corresponding spectrum in acid and vice versa. Compound **1** was adsorbed on to silica disks in order to investigate the gas-phase acid (or base) sensing properties of **1**. The disks were exposed to vapours of AcOH, TFA and HCl. In all cases it was possible to observe an increase in the emission of **1** adsorbed on the silica disk that was dependent upon the strength of the acid. For HCl and TFA vapours an increase of the emission intensity by a factor of 8 to 10 occurred, while for AcOH the emission intensity increased by a factor of about 4. Disks exposed to acid vapours (switch on fluorescence) were readily recycled by exposure to ammonia (switching off the fluorescence). The modified silica disks have shown that the material can be used up to 10 times without any change in the signal efficiency.

In short, the reported reaction is a simple, metal- and solvent- free alternative for the synthesis of **1**. The spectral properties of **1** were shown to be highly sensitive to both acids and bases in solution and in the vapour phase and thus exhibit promising sensing properties for detection of acids or amines in solution or in the gas-phase.

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2 L. E. Santos-Figueroa, et. al., *Chem. Soc. Rev.*, **2013**, 42, 3489.
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Poster Po15

Towards the obtention of bimetallic complexes: The case of [$Re(CO)_3(bpm)Br$] and [$BrRe(CO)_3(bpm)(CO)_3ReBr$].

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The development of novel bimetallic, or generally multimetallic, complexes has attracted increasing attention in coordination chemistry, mainly for two reasons: (i) they have interesting properties that cannot be attained with monometallic species, and (ii) they lead combination of functional molecules into one, for example, one metal center could be a photosensitizer while the other could be a catalyst.[1] In this sense, the [$Ru(bpy)_3$]$^{2+}$ or derivatives complexes has been widely studied as photosensitizer, due their photochemical activity, in the hydrogen evolution from H^+, photo induced CO_2 reduction and formation of C-C bonds in organic molecules, among others.[2] Ru^{II} shows favorable photophysical properties, that is: i) UV-Vis absorption ii) stable long-lived excited state and iii) effective excited state oxidant and reductant,[3] but it is not the only one at this respect. Among other metal complexes, [$Re^{I}(CO)_3$(diimine)X] type photosensitizers play a predominant role in last decade due to their useful and well defined properties that include stability, ^{3}MLCT excited states localized on the Re(NN) moiety and emission at room temperature.[4]

In order to develop new bimetallic systems, we present the synthesis, structure and photophysical properties of the mono and di-rhenium(I) species with the simplest bis-chelating diamine ligand, that is 2-2'bipirimidine (bpm), forming the [$Re(CO)_3(bpm)Br$] and [$BrRe(CO)_3(bpm)(CO)_3ReBr$] species (Fig. 1). They were prepared by the direct reaction of [$Re(CO)_3(THF)Br$]$_2$ and bpm at room temperature. The synthesis and structural characterization will be discussed, in addition to photophysical and electrochemical measurements and theoretical calculations in DFT and TD-DFT framework. These results will allow us to establish the principal differences when a second metal of the same type is inserted in an intramolecular arrangement and how much different it is compared to monometallic complex.

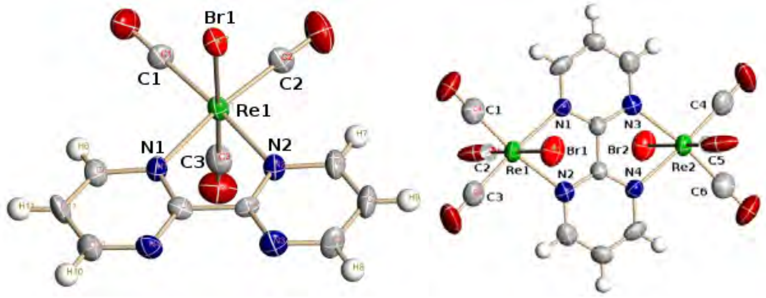

Fig 1. X-ray crystal structure (ORTEP images) of monometallic [$ReBr(CO)_3(bpm)$] *(left)* and homometallic [$ReBr(CO)_3(bpm)(CO)_3BrRe$] *(right)* complexes.

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Photophysical properties, Relativistic DFT Characterization and biological essays (walled cell models) of two new *fac*-Rhenium(I) tricarbonyl complexes.

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Research in fluorescence microscopy presents new challenges, especially with respect to the development of new d^6-metal-based fluorophores.[1-3] In this work, two new rhenium(I) tricarbonyl compound coordinated of 5,6-epoxi-1,10-phenanthroline (**Re1**) or diazofluorenone (**Re2**) has been synthesized, starting of bromotricarbonyl(tetrahydrofuran)-rhenium(I) dimer, leads to the monometallic complex, with good yield. **Re1** and **Re2** were characterized by FTIR, ^{1}H and ^{13}C NMR, DEPT, HHCOSY, elemental analysis and UV–vis spectroscopy in different organic solvents. The complexes show luminescent emission, and its photophysical properties were studied (lifetime, quantum yield, among the others).

This work also describes via relativistic DFT calculations, the electronic and spectroscopic properties of the *facial (fac)* and *meridional (mer)* isomers of this compound. The calculations shows that *mer*-isomer is higher in energy (in vacum and when the solvent is considered) with respect to the *fac*-isomer.[4] The calculated emission spectra of both **Re1** and **Re2**, indicates an emission in good agreement with the experimental data. The Morokuma–Ziegler energy decomposition analysis shows a major lability for -Br ligand which is ideal for designing new compounds replacing this ligand for another ancillary ligand, suitable for biological applications. Finally, we found that these compounds were less toxic than the ligand alone, and it depends on the cell model tested, where bacteria seem to be more susceptible than yeasts.[5]

Acknowledgements: We thank FONDECYT 11170637 and Núcleo UNAB DI-02-19/N for financial support.

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The role of the excited state dynamic of the antenna ligand in the Lanthanide sensitization mechanism

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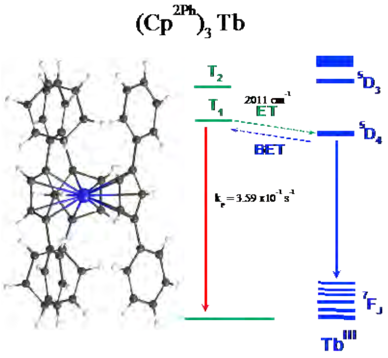
Lanthanides represent a family of multifunctional and strategic elements that are deeply involved in different scopes of human activity. Their unique electronic configuration provides these elements with unusual electronic, photophysical, and magnetic properties. The most relevant properties supporting several of the applications of lanthanide-based complexes relies on symmetry forbidden 4f-4f transitions. These transitions exhibit a very weak absorption, resulting, therefore, in a very weak luminescence. Accordingly, emission must be enhanced by attaching a suitably organic chromophore (ligands) to excite the lanthanide by the so-called “antenna effect” as a sensitizer. Thus, the antenna relaxes the strict selection rules resulting in significant luminescence enhancement. In this work an analysis of the sensitization of Tb^{3+} by a π-*bonded* antenna is presented. In general, the majority of the empirical rules that interconnect the efficiency of luminescent sensitization with the energy of the lowest singlet and triplet states of the ligand can be nonvalid in the case of π-*systems*, and due to that this is a relevant case from a theoretical point of view. In the work a detailed analysis of the excited state dynamic including the calculation of the radiative and no radiative constants is done in the framework of the multiconfigurational calculation of the states via CASSCF/NEVPT2 calculations. The effect of the vibrational states is also included regarding the Franck-Condon factors and Herzberg-Teller effect.



Interfacing Perovskite nanocrystals for efficient charge transfer

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Perovskite nanocrystals have garnered much attention in the past decade for their ability to harvest solar energy. In fact, solar cell efficiencies of perovskite films have increased at an unprecedented rate from 3.8% in 2009 to 22.7% in 2017. Even with these advances, perovskites are known for their instability in polar media making solution-based experiments challenging. Much is to be discovered in regard to interfacing the perovskite surface and improving their stability in colloidal solutions.

In this work we focus on the all-inorganic $CsPbBr_3$ perovskite nanocrystals. Their large surface-to-volume ratios are beneficial for investigating interfacial charge transfer (CT) between the nanocrystals (as electron acceptor) and small organic conjugates (as electron donors). Aliphatic amines have propensity for binding to surfaces of perovskite materials. Therefore, we select ethyleneamine derivatives of phenothiazine (PTZ), along with their analogues lacking the amines, for electron donors. Phenothiazines have sufficient driving force for hole transfer at 300 meV. We observe photoluminesce quenching only when the amine derivatized PTZ is present in solution. Trap passivation is also observed only in the amine functionalized PTZ. Slow charge transfer rates lead us to believe the ethylene linker greatly slows CT regardless of binding affinity. These results demonstrate that the binding affinity to the inorganic surface decisively affects the interfacial charge transfer. Using the ethyleneamine derivatives of the same donors further confirms the importance of binding affinity. To preserve the integrity of the perovskite nanocrystals, we employ hydrocarbon solvents. Nevertheless, we observe charge-transfer quantum efficiency of about 90% even in such non-polar media.

Additionally, the concentration of the donor plays a significant role in maintaining both colloidal stability and structural integrity of the perovskite nanocrystals. Aggregation is found to occur when the nanocrystals are subjected to excessive donor concentration.

These findings provide important paradigms for interfacing perovskites with organic conjugates.

Poster Po19

Micro-morphological effects on the photocatalytic properties of TiO_2 films immobilized onto glass slides

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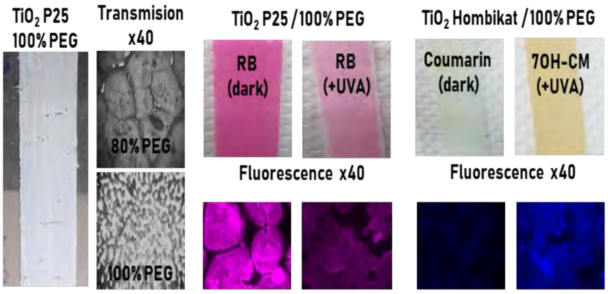
Titanium dioxide (TiO_2) is the most popular semiconductor utilized in photocatalytic processes, including water-splitting and contaminant degradation.[1] The low cost and toxicity, high thermal and chemical stability of TiO_2 are still advantages for its use as photocatalyst applying different immobilization strategies , despite the requirement of using UVA illumination sources for photoexcitation of the conductive band (3.1 eV).

In this report we present a systematic study of the photocatalytic efficiency of TiO_2 thin films prepared by the “Doctor Blade” technique onto commercial microscope glass slides. For this purpose 1 g of commercial TiO_2 powder (Degussa P25 or Hombikat) was homogenized with 100 µL of acetyl acetone, 50 µL of sodium dodecyl sulphate (10 mg mL^{-1}), and different amounts of polyethylene glycol (PEG 20000, 20-100 %w/w TiO_2) and latter, were calcinated during 2 h at 450 °C. The immobilized TiO_2 were characterized by UV-vis reflectance and ATR-FTIR spectroscopies as well as by optical transmission and fluorescence microscopy.

All films were mechanically stable after immersion in a water bath with orbital agitation during 5 h, while the %PEG has not effect on the amount of TiO_2 deposited. However, different micro-morphology patterns were observed as a function of the PEG composition. Also, the photocatalytic activity of the films were evaluated by irradiation with a germicidal lamp (λ_{max} 365 nm) and monitoring both the bleaching of adsorbed xanthenic dye Rose Bengal (RB)[2] and reaction of the pre-fluorescent probe coumarin (CM) with the photo-generated $HO^{\bullet}$, to form 7-hydroxicoumarin (7OH-CM), which shows fluorescence at 460 nm.[3] The relative quantum yields of RB photobleaching and $HO^{\bullet}$ generation are discussed as function of the surface micro-morphology of the TiO_2 films.



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Photocatalytic Activity of Titania: Study of Different Anatase/Rutile Ratios.

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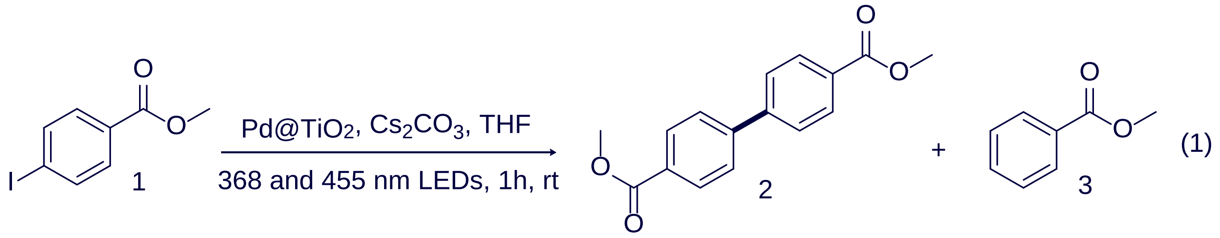
Titanium dioxide (TiO_2) exists as three polymorph phases at atmospheric pressure: anatase, brookite and rutile. These phases have different crystal structures and consequently, different properties[1]. Rutile is thermodynamically stable compared with anatase and brookite. These two forms can be transformed into rutile by heating at high temperature[2]. Despite its unstableness, anatase has shown a higher photocatalytic activity compared with rutile[1].

Several works have investigated the photoactivity of anatase and rutile and, in many examples, catalysts with more weight-fraction of rutile have been more active.

For instance, it has been reported that TiO_2 microspheres with a rutile weight fraction of 50 % show the highest activity for the photodegradation of organic pollutants as methylene blue, rhodamine B and methyl orange in aqueous solution[3]. Also, a mixed-phase TiO_2 powder with 40 wt% rutile exhibits the higher photocatalytic activity for the degradation of methylene blue[4]. Finally, TiO_2 sub-micron fibers with 38 wt% of rutile phase have the optimal initial degradation rate constant for the photodegradation of phenazopyridine, a pharmaceutical contaminant[5]. In general, these studies concentrate on the material's ability to photodegrade organic compounds. In contrast, here we focus our efforts to evaluate the photocatalytic activity of the different rutile fractions to accelerate organic reactions; in particular, the well-known Ullman reaction. For that we utilize a series of home-made palladium-doped titania (Pd@TiO_2). Thus, the homocoupling (eq. 1) of 4-methyl iodobenzoate (1) was carried out in THF with 2 eq. of base and irradiated with 368 and 465 nm LEDs working at 0.4 and 1.9 Wcm^{-2} respectively, for 1 h and at room temperature (rt). We fully characterize the materials by means of X-ray diffraction, RAMAN and Diffuse reflectance spectroscopy and ICP-OES**.** Overall, we find optimal rutile ratios for the reaction.



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Poster Po21

Comparison of different anthocyanin-metal complexes as photosensitizers in DSSC

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Dye sensitized solar cells (DSSC) are photoelectrochemical devices that resemble natural photosynthesis because they use an organic dye to absorb light and produce a flow of electrons [1]. A DSSC consists of a semiconductor TiO_2 which is covered with a monolayer of dye molecules. The semiconductor is deposited onto a transparent conductive oxide electrode, through which the cell is illuminated. The pores are filled with a redox electrolyte that acts as a conductor and that is electrically connected to a platinum electrode. [2]

Today, many types of research are conducting around the search for the best dye to improve energy efficiency conversion. For that reason, the use of natural dyes is an attractive alternative, especially for emergent countries because of the low cost of fabrication of cells based on their use, besides the environmental benefits related to their employment.

According to our previous results in the laboratory, the anthocyanins of the ceibo flower have promising characteristics to be used in Graetzel cells. However, these red anthocyanins have only one limiting factor: they can only absorb light in a narrow area of the visible spectrum.

In this work, we evaluate the formation of anthocyanins complexes with a metal ion, Mn^{2+}. The generated chemical compounds presented a different color depending on the pH and the stoichiometric ratio between the dye and the metal ion.

These compounds obtained were characterized by UV-visible and cyclic voltammetry. Additionally, thermal studies were carried on in order to evaluate the stability of the different complexes.

After that, some cells were assembled with anthocyanin-metal complexes and also with a mixture of these complexes and free anthocyanins, evaluating its performance through electrochemical techniques, as IV profiles. These studies allowed us to obtain and compare the efficiency values of the energy conversion and the fill factor of the different cells to conclude which dyes will be suitable for the use we propose.

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Poster Po22

The First observation of Azo-Hidrazone tautomerism for Rhenium (I) Tricarbonyl Complexes.

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Tautomerism is a process of exchange of a proton between two or more forms, hence, it leads to rearrangement of the electronic density in the molecule and produces significant changes in the spectral and photophysical behaviors.[1] In some cases, azo dyes are also referred to as hydrazone dyes since they can be either in the azo or in the tautomeric form.[2] Azo dyes and their metal complexes are important chromophores in dye chemistry and their applications are strongly dependent on their properties. For instance, photophysical properties of azo-hydrazone tautomerism have been used for dye location characterization in surfactant micelles, photographic systems, dyeing and bleaching.[3]

Photophysical properties of the azo-hidrazone tautomerism of Rhenium (I) tricarbonyl metal complexes were investigated using UV-Visible and ^{1}H NMR spectroscopy. The effects of varying pH, dye concentration, solvent, and time-dependences on the UV-Visible spectra of these metal complexes were also investigated.

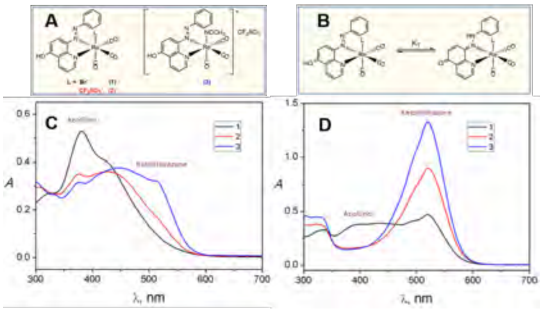

Figure 1. A) Rhenium tricarbonyl complexes under study, B) tautomeric equilibrium, C) UV-Visible spectra of Rhenium (I) complexes in dry acetonitrile, D) UV-Visible spectra of Rhenium (I) complexes in dry DMSO

We observed that the tautomerization process is strongly influenced by the nature of solvent, pH and temperature, as observed in pure organic molecules. Nevertheless, the change of the electronic density in the organometallic fragment by substitution of the ligand L, is the determining factor in the tautomerization of the metal complexes under study (**Figure 1**).

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Acknowledgments:

Postdoc Fondecyt 3180488

“Método biomimético, simple y económico para síntesis de nanopartículas de CuInS$_2$ con emisión en IR-cercano y sin fototoxicidad”

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Las nanopartículas fluorescentes o “quantum dots” (QDs) han resaltado en el último tiempo debido a su uso en televisores (quantum dotdisplay), celdas solares y bioimagenes. Los QDs emiten fluorescencia de distintos colores al ser excitados a una única longitud de onda, presentan gran resistencia a la foto-degradación (especialmente en comparación a fluoroforos orgánicos) y pueden ser conjugados a distintas bio-moléculas lo que permite modular sus propiedades.

Nuestro laboratorio se ha interesado en el estudio y la aplicación de nano-materiales de cobre y litio. En este sentido, las nanopartículas de CuInS$_2$ (CIS) representan una interesante alternativa debido a sus propiedades únicas que favorecen sus aplicaciones: absorción de la luz en luz visible he infrarrojo cercano y fluorescencia en el infrarrojo cercano (útil para bioimagenes y para captar fotones en celdas solares), acompañando a esto una banda prohibida (band gap) entre 1,5 – 2 eV y su baja toxicidad.

Actualmente la síntesis de estas nanopartículas (NPs) se realiza mediante métodos químicos, los cuales involucran altos costos de producción y condiciones de síntesis complejas. A la fecha, no se han descrito métodos biomiméticos estas nanopartículas. Debido a esto el objetivo de este trabajo es obtener NPs de CuInS$_2$ mediante síntesis biomimética que representa un método de síntesis verde.

Hemos desarrollado un método biomimético de síntesis de CIS que involucra ambiente acuoso, bajas temperaturas (80ºC) y presión atmosférica. Este método involucra el uso de sales de Cu e In, además de glutatión como fuente de S y estabilizante de las NPs. Las NPs producidas emiten fluorescencia en el rango sobre los 650 nm al ser excitadas a 500 nm. Mediante TEM se determinó que el tamaño de las NPs es cercano a los 30 nm. El análisis de EDS confirmo que las NPs están compuestas efectivamente por Cu, In y S. EL análisis de XRD determinó que presentan el patrón de difracción de las NPs de CuInS$_2$, aunque falta mejorar su cristalinidad. Las NPs fueron incorporadas en celdas solares lo que confirmo su capacidad de actuar como fotosensibilizadores captando fotones.

Por otro, lado también se determinó el MIC para Escherichia coli de las nanopartículas sintetizadas, el cual fue de 30 mg/ml siendo muy poco tóxicas compara con otra nanopartícula sintetizada por métodos biomiméticos como lo son las de CdTe-GSH que tienen un MIC de 2 mg/mL, además ensayos realizados sugieren que no tienen un efecto fototóxico en la bacteria E. coli cuando se irradian con un láser a 530 nm.

En conclusión, se logró obtener un método de síntesis verde de NPs de CuInS2. Mediante este método se estableció un protocolo fácil, reproducible y económico, el cual se caracterizó y confirmó la formación de NPs de CuInS$_2$ y siendo no toxicas y con muy poca fototoxicidad en las condiciones probadas para E. coli.

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Poster Po24

Cinnamoyl–coumarin derivatives with remarkable fluorescent molecular-rotor properties for the detection of domains in mixtures of DPPC/DOPC LUVs.

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We have design and synthesized cinnamoyl–coumarin probes with different hydrocarbon chain length (C_{334}-C_nH_{2n+1}) capable of testing the presence of lipid microdomains in LUVs liposomes using DPPC:DOPC phospholipids. The photophysical analysis using stationary and time-resolved spectroscopies showed larger bathochromic and stock shifts in polar solvents but a decrease on the fluorescent quantum yields. Theoretical calculus have allowed us to explain that photophysical behavior of C_{334}-C_nH_{2n+1} associated to the formation of a twisted intramolecular charge transfer (TICT). Thus, these probes behave as fluorescent molecular-rotors due to the dependence of the TICT excited state properties to constrain environments in liposomes responding to the membrane fluidity in different compositions of lipid mixtures in of DPPC:DOPC (Figure 1). Furthermore, time-resolved fluorescence anisotropy showed different rotational lifetimes depending on the hydrocarbon chain length suggesting different localization of these probes in lipid domains. These results are in agreement with the most favorable orientation of cinnamoyl–coumarin derivatives determined in membrane models by molecular dynamics.

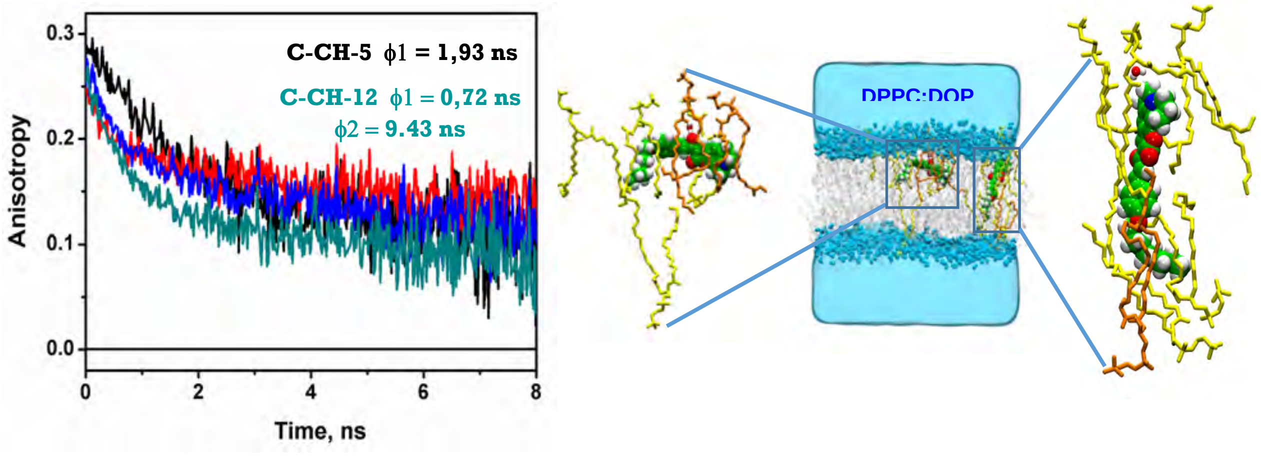

Figure 1. (A) Time-resolved anisotropy of cinnamoyl–coumarin derivatives in liposome of DPPC:DOPC, at 22°C under atmosphere of N2.(B) The most favorable orientation of C-CH- 8 in membrane model of DPPC: DOPC (1:1).

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Poster Po25

Investigations of photophysical properties of new phenotiazinium photosensitizers to induce membrane damage

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Photosensitizers (PS) based on the phenothiazinium chromophore have been extensively explored to improve the photodynamic therapy (PDT) to promote cancer activity, photodisinfection and photoinduced membrane damage. Phenothiazinium cations, as MB, methylene blue, are composed of an oxidized ring system chromophore and attached auxochromic side groups which different substituent that perform differences in their polarity and hydrophobicity properties. In this way, studies related with structure-activity of these PSs are important to further understand the PDT mechanisms. Recently our research group elucidated the mechanism that lead to photoinduced membrane damage by a class of phenothiazinium PSs (DO15, DMMB, MB, TBO). The studies showed that membrane damage mechanism involves more than singlet oxygen ($^1O_2$) production by PSs, but the efficiency of the PSs is related with direct contact reaction with the lipids bilayers. The lipid oxidation by PSs leads to an aldehyde formation product that open pores in the membranes and lead to the leakage of the contents of the cell or its organelles. This study also confirm that PSs structures arrangement play a major role in their efficiency to promote membrane damage, which lead DO15 permeabilize membranes 1 order of magnitude more efficiently than MB and this is associated with higher colocalization of DO15 in lipid double bonds than MB. In this way the PSs photoinduced mechanism in membrane damage is important to the development of more efficient molecule to destroy the organelle membrane. In this direction the current work aiming to compare different properties of a series of phenothiazinium salts composed by MB, DO15, DO16 and DO37 in terms of their structure-activity in the ground and excited states of the PSs in the membrane models. We are interested not only at the properties of PSs in induced membrane damage (showed by leakage of a fluorescent probe and generation of products of lipid oxidation) but also to understand the changes in the membrane lipids bilayer that shows the great importance in specificity actions in light induced process with membrane. PSs have molar absorptivities of ~10^4 M^{-1} cm^{-1} and absorption maxima between 650 - 670 nm, Φf values lower than 0.1 and high Φ_Δ, around 0.5. The $^1O_2$ lifetime of the PSs showed that not occurs quenching in $^1O_2$ formation. The membrane/solution partition of PSs showed that DO15, DO16 and DO37 bound to membranes greater than MB. Although other parameters are important to explain membrane binding the higher polarity of (DO) PSs contributed more to their efficiency membranes binding. To further compare the efficiencies of PSs in photoinduced membrane damage, liposomes containing the self-quenched fluorescent probe CF (5,6-carboxyfluorescein) were irradiated ($\lambda = 630$ nm) for up to 180 min in the presence of PSs. After irradiation time CF fluorescence increased greater for DO class than MB and its showed faster CF leakage for DO15 and DO37. The dark control showed no significance values of CF fluorescence in 180 min. In this way additional study has been performed based in membrane protocols to better elucidate the mechanism involved in this photoinduced membrane damage by the phenothiazinium PSs and the relationship between their activity-structure properties.

Poster Po26

Lysozyme bionanoparticles formed by blue-light sensitized crosslinking: mechanistic insights

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Photo-induced protein modification can occur via multiple pathways, involving free radical and reactive oxygen species inducing redox reactions mainly of Trp, Tyr, Cys, Met and Hys residues.[1]

In this work, we studied the photosensitized modification of lysozyme (LZ) by blue-light excitation of the ruthenium II complex $Ru(bpy)_3^{2+}$ in the presence of a molar excess of $S_2O_8^{2-}$ as a sacrificial electron acceptor.[2] Photolysis was performed in N_2- or air-saturated buffered solution (pH 7.4) up to 20 min by irradiation with a Royal blue LED (462 ± 14 nm). The reaction was monitored by absorption and fluorescence spectroscopies, laser-flash photolysis, SDS-PAGE and dynamic light scattering analysis, mass spectrometry and also by transmission electronic microscopy.

Steady-state spectroscopic changes and MS analysis indicated the efficient formation of protein degradation products, such as di-tyrosine, kynurenine, and quinone derivatives of both residues. The formation of di-tyrosine was favored in N_2-saturated solutions. LFP experiments in air-saturated solutions confirmed the efficient quenching of the triplet state of $^3Ru(bpy)_3^{2+}$ by $S_2O_8^{2-}$ to form $Ru(bpy)_3^{3+}$ and $SO_4^{\bullet-}$, a strong oxidizing and hydrogen atom abstracting agent.[1] In presence of LZ, the changes of the transient absorbance indicated the recovery of the sensitizer due to the reduction of $Ru(bpy)_3^{3+}$ and the disappearance of $SO_4^{\bullet-}$ to SO_4H^-. The photoreaction generates the progressive formation of covalent protein oligomers (e.g. dimer, trimer, …*n*-mer) as detected by SDS-PAGE and dynamic light scattering (DLS), determining a size particle increase from approximately 6 to 14 nm. TEM images confirmed the presence of larger globular aggregates after photolysis treatment. Finally, the oligomeric species of LZ showed slight UVA-photosensitizing capability, with singlet oxygen quantum yield of ≈2%, as determined by the O_2-uptake with triptophan and Trp-uptake induced photo-oxidation experiments.

In summary, blue-light mediated photosensitization of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ mixture produces soluble oligomeric bionanoparticles of lysozyme that can be used as medical drug and/or dye photosensitizer vehicle for biomedical applications.

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Poster Po27

Photophysical and photochemical characterization of inclusion compounds of methylene blue with cucurbiturils and cyclodextrins

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Common photosensitizers (PSs) used in photodynamic therapy (PDT) have shortcomings that pose challenges for their wide applications in medicine. Most of the current PSs are highly conjugated compounds that usually suffer from low water solubility or strong aggregation abilities in aqueous solutions, both of which lead to the low photodynamic activities. Moreover, the "always on" photoactivity and slow *in vivo* clearance of the most common PSs could lead to potential post-treatment risks associated with harmful photosensitization effects on eyes, skin and other normal tissue[1]. In recent years, a great effort has been made in developing ways to overcome these drawbacks. Investigations in this area have led to a novel ''supramolecular'' strategy for developing new and smart PSs. Supramolecular PSs utilize non-covalent intermolecular interactions to construct PDT active assemblies. This effort has led to the development of unique PDT agents that are comprised of self-assemblies of the same molecular PSs, co-assemblies of different molecular PSs, co-assemblies of molecular PSs with other small non-PS molecules, and non-covalent nano-systems consisting of molecular PSs and additional materials. Non-covalent interactions endow supramolecular PSs of these types with controllable photoactivities[2].

In this work, we report the photophysical and photochemical characterization of inclusion compounds of methylene blue with cucurbiturils (CB[7] and CB[8]), acyclic cucurbiturils (M1C4 and M2C4) and cyclodextrins (β-CD and γ-CD). We determined the association constants of the inclusion compounds and the thermodynamic parameters of the inclusion process by isothermal titration calorimetry (ITC). Photophysical changes were studied by UV-Vis and fluorescence spectroscopy. Singlet oxygen was detected by the bleaching of ABMA using UV-Vis and fluorescence spectroscopy.

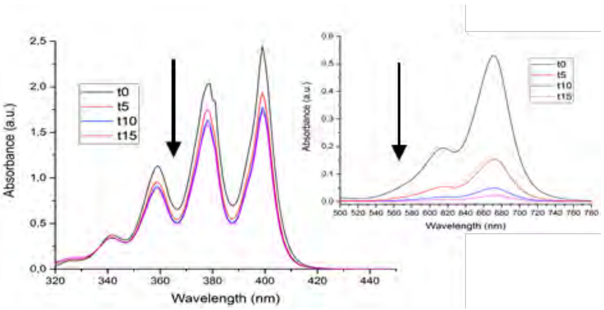

Fig. 1: UV-Vis spectra for the bleaching of ABMA (200 μM) due to singlet oxygen generation by MB (15 μM).

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Poster Po28

Stability of anthocyanin of the crude extract of *Hibiscus sabdariffa L* in different means of dispersion

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Anthocyanins, natural pigments of the flavonoid class, are present in several plants, most often in flowers and fruits. They are water soluble species and have many health beneficial properties. However, its use as a food coloring is limited due to its stability, being susceptible to factors such as pH, temperature, light and oxygen. The main objective of this work was evaluate the stability of anthocyanins from extract of Hibuscus sabdariffa L. (HS), against pH variations and presence of cellulose and starch biopolymers derivatives (Carboxymethylcellulose – CMC, Hydroxyethylcellulose HEC e potato starch - AMP).

The dehydrated HS petals, ground and sieved, were dispersed in ethanol/water mixtures (30, 50 and 70%), at a concentration of 20 g/L, at 25ºC for 1h. The material was centrifuged and filtered. Anthocyanins were quantified by the differential pH method [1-2].

The half-life ($t_{1/2}$) of the degradation kinetics of anthocyanins present in the crude extract was used to monitor stability by monitoring molecular absorption spectrum with a Varian Cary50 spectrophotometer. Aliquots of the extract, 1/10 (v/v), were added in solutions with pH from 1 to 8 and monitored for 13 hours. Similarly, aliquots of the extract, 1/10 (v/v), were added in CMC, HEC and AMP solutions at concentrations of 0.50%, 0.25% and 0.01% (w/v) and monitored at 25ºC, 50ºC and 75ºC.

The results indicate that the highest total anthocyanin content, 7.2635 ± 0.0980 mg.100g^{-1}, was obtained in the ethanol/water mixture 50%.

In the presence of biopolymers, the half-life of the extract pigments were even longer. In the solutions of the biopolymers tested, CMC, HEC, AM-APC, the best results were obtained at a concentration of 0.01% at 25ºC, at pH 4, with a half-life of 23.90, 33.96 and 53.32 hours, respectively.

The results suggest that the cellulose and starch derivatives biopolymers significantly increase the half-life of the pigments present in the crude extract of Hibuscus sabdariffa L., showing a stabilizing effect much higher than the pH effect. Other related studies on the effect of the environment on species stability are underway.

Aknowledgement: Fapesb and Finep for the financial support.

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Poster Po29

DPPC/Dox liposome functionalization with Cell Penetrating Peptide for Drug Delivery

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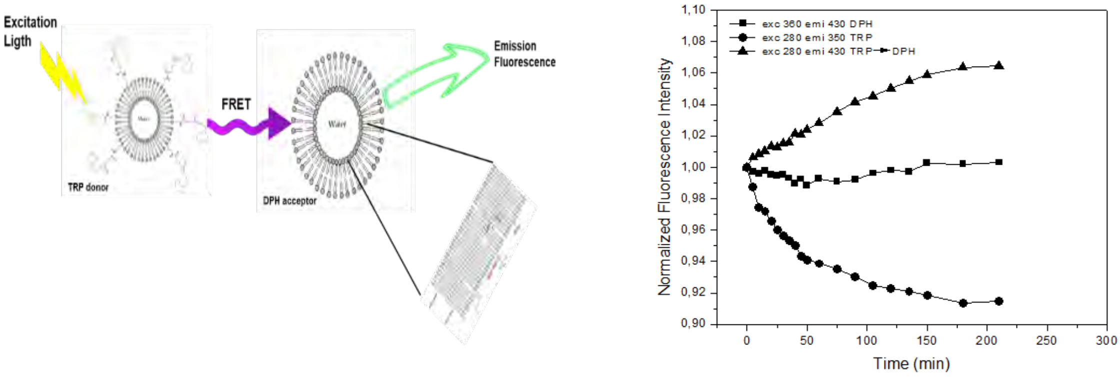
Dipalmitoyl phosphatidyl choline (DPPC) unilamellar vesicles have been widely studied as a transport and drug delivery systems. In this context, the presence of effective and external vectors has allowed the generation of new alternatives for the efficient drug delivery. Cell penetrating peptides, CPPs, have been studied to promote the release of drugs from liposomes[1].

The aim of this study is to show that through of DPPC liposome functionalization with CPPs, an increase of Doxorubicine (Dox) incorporation in HeLa cells will be observed.

DPPC liposomes in the presence of N-glutaryl-PE were prepared by the extrusion method through a polycarbonate filter with 200nm nominal pore, after five freezing/thawing cycles in PBS buffer 10mM pH 7.4 in the presence of Dox. Free Dox, not encapsulated into DPPC liposome, was separated by exclusion chromatography column using sephadex-G50. Liposome/Dox were functionalized through activation of NGPE carboxyl group, once activated, it was incubated with CPPs for 24h at 24°C. Free CPPs was separated using sephadex-G50. The functionalization of DPPC/Dox liposomes was evidenced by fluorescence energy transfer experiments (FRET) between Trp emission and DPH fluorescent probe and Trp fluorescence quenching by acrylamide.

The main results showed that DPPC liposomes can be functionalized with CPPs, and cell viability of HeLa cells depend on DPPC and Dox concentration. Functionalization of DPPC/Dox liposomes with MPPs resulted in an increase of Dox incorporation in HeLa cells after 3h and 5h of incubation at 37ºC.



<u>Figure 1</u>: General overview of FRET experiment between Trp of CPPs and DPH. Right hand, normalized fluorescence intensity of DPH and Trp in the presence of acrylamide. Exc 280nm (-●-) Trp emission, (-▲-) DPH emission and (-■-) Exc360/Em430nm of DPH.

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Assessment of an extrinsic chromophore-labeling peptide with DPPC, DOPC, DPPC:DOPC and POPE:POPG lipid membranes.

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A 15-residues peptide (CUM-KWKLFKKIGAVLKVL-NH_2) with a coumarin-343 in the N-terminal was synthesized by the solid phase (SPPS) methodology (Figure 1A), and an acetylated in the N-terminal peptide as a control peptide. The behavior of these peptides in lipid membrane models was evaluated. For this purpose, large unilamellar vesicles (LUVs) of the zwitterionic phospholipids DPPC, DOPC and DPPC:DOPC (50:50%), were synthesized as models of mammalian lipid membranes. In addition to this, LUVs of negatively charged phospholipids POPE:POPG (70:30%) were synthesized as a bacterial lipid membrane model.

In order to characterize the interaction peptide/lipid bilayer, fluorescence and fluorescence anisotropy techniques, both in steady-state and time-resolved modality were performed. Additionally, circular dichroism measurements were carried out to assess the conformational change of the peptides within the lipid bilayer.

Both peptides were monomers and random-coil in aqueous medium, but changed their structure to α-helix (Figure 1B), in the case of liposomes of DOPC and DPPC:DOPC (50:50%); but acquired a polyproline-II type conformation (PPII) when inserted into liposomes of POPE:POPG (70:30%), as observed by circular dichroism measurements. In LUVs of DPPC, none of the peptides were inserted into the lipid bilayer, due to this membrane is in gel state at the temperature of measurement (293 K), as observed by fluorescence spectrophotometry and circular dichroism.

It was noted the existence of three lifetimes, a $\tau_1 = 0.17\text{-}0.27$ ns assigned to a quenching mechanism between the fluorophore and the peptide chain. A second lifetime, $\tau_2 = 0.89\text{-}1.79$ ns, was attributed to the formation of a locally excited (LE) state, and a third lifetime $\tau_3 = 3.70 - 3.84$ ns which is associated to an internal charge transfer (ICT) state. In addition to this, time-resolved fluorescence anisotropy measurement revealed a fast component for the fluorophore coumarin-343 in water of 0.92 ns ($\lambda_{ex} = 295$ nm), indicating free rotational diffusion. nevertheless, in the presence of DOPC and POPE:POPG, two rotational correlation times, $\theta_1 = 0.5\text{-}1.0$ ns, assigned to the rotational diffusion of the chromophore moiety and a long time $\theta_2 = 15\text{-}37$ ns, attributed to slow movements of the helix within the lipid membrane.

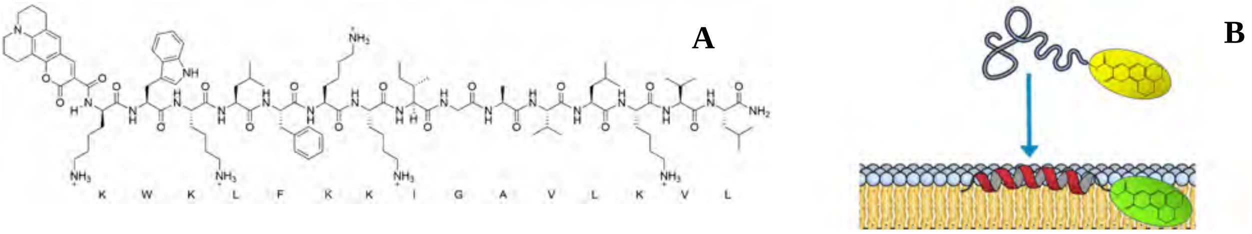

Figura 1. (A) Primary structure of the coumarin-labeled peptide. (B) Conformational change of the peptide in aqueous medium and a lipid-bilayer (random-coil → α-helix)

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Photochemistry of aryl benzoates in mro-heterogeneous media

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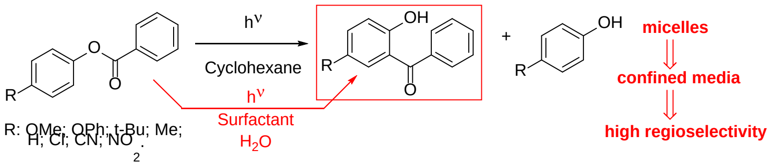
The photo-Fries rearrangement was discovered by Anderson and Reese in 1960[1] and the photophysical and photochemical aspects of the photoreaction have been studied.[2] Successful application of the photoreaction in organic synthesis has also been attempted, for example, in the total synthesis of murrayacine, daunomicine and tetracyclines.[2] However, the photo-Fries rearrangement of aryl benzoates has scarcely been investigated.[2] Interestingly, 2-hydroxybenzophenone derivatives can be obtained from the photo-Fries rearrangement reaction of aryl benzoates. These benzophenone derivatives can be used as photochemical filters in solar creams, as possible actinometers due to their photochemical stability and also, in the synthesis of building blocks of natural products. The structure of the esters and the photochemical reaction are shown in Scheme 1.



Scheme 1. Photo-Fries rearrangement of aryl benzoates.

Herein, we present the results obtained during the irradiation of aryl benzoates in cyclohexane and micro-heterogeneous media by means of steady-state and time-resolved spectroscopies. First of all, a series of *p*-substituted phenyl benzoates were prepared and fully characterized by physical and spectroscopical methods (pf, NMR). Then, preparative photochemical reactions of the aryl esters were carried out with UV light (254 nm) in cyclohexane leading to isolate from the reaction mixture and fully characterize by NMR spectroscopy the 2-hydroxybenzophenone derivatives. Three different surfactants were used to build up the micellar solutions of the aryl esters: SDS (anionic surfactant), Brij-P35 (neutral surfactant) and CTAC (cationic surfactant), and the micellar solutions were also irradiated at 254 nm. A high regio selectivity of the photoreaction was observed in these media favoring the formation of 2-hydroxybenzophenone derivatives up to 98 % yield. Quantum yields of consumption of the aryl esters (ϕ_r) were also measured in both media affording higher values of ϕ_r in micellar solutions than in cyclohexane. Likewise, the constants of binding (K_b) were measured in presence of the surfactants giving values between 70 and 1700 M^{-1} depending on the nature of the substituent attached to the aryl moiety of the esters as well as the kind of surfactant used. Finally, 2D NMR spectroscopy (NOESY experiments) of an aqueous solution of the aryl benzoates and each surfactant was performed in order to show that the aryl benzoates are located within the core of the micelles. Finally, irradiation of some representative esters in cyclohexane and micellar solutions with a laser pulse of 266 nm led to the characterization of the transient *p*-substituted phenoxyl radicals as well as the 2-benzoylcyclohexadienones which are the responsible for the observed product distribution of the photoreaction.

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Conjugated Polymer Nanoparticles as Coinitiator- Free, Water-Soluble, Visible-Light Photoinitiators of Vinyl Polymerization

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Free-radical photopolymerization reactions are extensively used in many industrial processes. These processes involve a polymerizable mixture composed by one or more vinylic monomers and a photoinitiator system (PIS) able to generate radical species using light as energy source. PIS are generally classified into two main categories: *Type I PIS* produce free radicals through the homolytic cleavage of C-C or C-X bonds usually under UV irradiation. *Type II PIS* comprise at least two components: a photosensitizer that absorbs UV or visible light and a co-initiator that serves as electron or hydrogen donor.

We report herein the use of conjugated polymer nanoparticles (CP NPs) of poly(9,9-dioctylfluorene-altbenzothiadiazole) (F8BT) and poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) as efficient photoinitiator systems (PIS) for vinyl polymerization in water. CP NPs are biocompatible, excitable with blue commercial LEDs (~450 nm) and, unlike visible light Type II PIS, do not need co-initiators to trigger monomer chain reaction. CP NPs photoinitiate polymerization of a variety of acrylic monomers with initiation rates comparable to those observed for well-known Type II PIS. Given the extraordinarily large molar absorption coefficients of CP NPs ($\varepsilon = 10^8$ M^{-1} cm^{-1}) very low particle concentration is required for effective polymerization (~5-20 ppm of polymer or what is equivalent ~10-40 nM in NPs), making these PIS suitable to synthesize polymeric materials for biomedical and other applications. CP NPs photoinduced polymerization was studied using different techniques such as FT-NIR, Dynamic Light Scattering (DLS) and fluorescence microscopy Single Particle Tracking (SPT). CP NPs PIS were also used to synthesize hydrogels and nano-hydrogels with relatively narrow and controlled size distribution in the absence of surfactants. The use of different types and proportion of monomers and crosslinkers with these novel PIS allows the preparation of polymer NPs useful for a number of technological applications such as: drug delivery, selective sensing/removal of molecular targets (molecularly-imprinted nanopolymers), fluorescent probes for imaging of molecular targets in biological systems, etc. Although the photoinitiation mechanism could not be fully established, experimental evidence suggests that polymerization is initiated at the CP NPs surface by photogenerated free polarons in close analogy to the mechanism proposed for PIS based on inorganic semiconductor NPs.

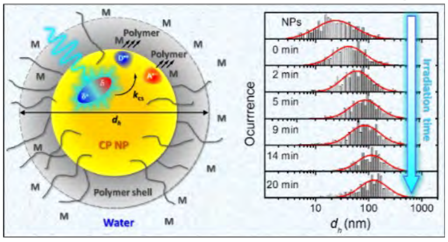

Figure 1. Schematic representation of the photoinitiation mechanisms of vinyl polymerization by CP NP **(**Left). F8BT NPs size distribution measured by SPT during polymerization of an HEMA/BAAM mixture photoinitiated using F8BT NPs 12 ppm (Right)

Cholesterol effect on membrane fusion of lipids vesicles mediated by Infectious Salmon Anaemia Virus Fusion Peptides

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Infectious salmon anaemia virus (ISAV) is known to cause health problems to the salmon aquaculture industry. The entrance of ISAV into host cells is facilitated by the insertion of a hydrophobic segment of the ISAV fusion protein called fusion peptide. This mechanism is crucial for infection, but role of lipid content and the lipid phase packing order of membranes on the virus fusion mechanism are still unclear.

In this study, the effect of cholesterol on the membrane fusion mediated by ISAV fusion peptides was analyzed in LUVs and GUVs. In addition, the fusion peptides were synthesized by standard Fmoc-methodology and the fusion assays were performed using large unilamellar vesicles (LUVs) of ternary lipid mixtures containing different mole fractions of cholesterol.

Secondary structure changes of the ISAV fusion peptides when they interact with the vesicles with different cholesterol content were analyzed by circular dichroism. The results of secondary structure in lipids vesicles show that ISAV fusion peptides adopt a β-sheet conformation. The dissociation constant (K_d) of the peptides was obtained using the tryptophan steady state fluorescence anisotropy technique present in the peptides. We also studied the interactions between GUVs and peptides-TRITC by confocal fluorescence microscopy.

We evaluated the effect of the cholesterol content on the phospholipid acyl chain packing order of vesicles. The anisotropy of DPH and TMA-DPH was studied on LUVs with mixtures of 1:1 DOPC/DPPC with 0, 15, 20 and 33 mol% cholesterol in absence and presence of ISAV fusion peptides.

On the other hand, LUVs were prepared with dipicolinic acid (DPA) and terbium for demonstrate formation of the fusion pore by formation of the fluorescent complex $Tb(DPA)_3$. The kinetics of hemifusion was studied by fluorescence-dequenching assays used octadecyl rhodamine B. Our results showed that the cholesterol content of the LUVs (0,2 µm of diameter) affects the fusion of the membranes mediated by ISAV fusion peptides, obtaining a greater kinetics of membrane fusion in the absence of cholesterol.

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Different Strategies to Synthesize Hybrid Nanogels by Photopolymerization Employing Conjugated Polymers Nanoparticles and Silsesquioxanes

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The design and preparation of nanogels have attracted a great deal of interest in biomedical engineering, pharmaceutical applications, and in biomaterials science. Nanogels have certain advantages over macro hydrogels such as: controlled administration of bioactive agents at specific sites, low toxicity, and high biocompatibility, among others[1]. On the other hand, nanogels can be combined with other materials to generate hybrid systems and thus improve and/or establish better specific properties. Among all the synthesis paths to achieve nano materials, inverse mini emulsion polymerization seems to be the most used technique to synthesize nanogels from hydrophilic monomers[2]. Nevertheless, the employment of organic solvents and the use of surfactants represent disadvantages associated to this technique. Because of these drawbacks, some new techniques have been investigated to overcome these issues. In this work two different successful ways to synthesize nanogels are presented: *inverse mini emulsion photopolymerization* and *precipitation*. In both cases conjugated nanoparticles as macrophotoinitiators (CPNPs) were employed.

Nanogels of 2-methacryloyloxy ethyl trimethyl ammonium chloride (METAC) and 2-hydroxyethyl methacrylate (HEMA) containing a silsesquioxane precursor in their structure that act as crosslinker and co-iniciator were synthesized by both methods. The photoinitiator system consists of conjugated polymers nanoparticles of F8BT or PFO. Also, monomer, surfactant, crosslinker and CPNPs concentrations were varied to obtain nanogels with different diameter by both methods.

CPNPs have the capacity to absorb and emit radiation in the visible region of the electromagnetic spectrum; and to participate as an electron transfer agent, thus initiating the polymerization by visible light without a sensitizer. In addition, CPNPs are retained in the nanogel matrix after polymerization, which represents an advantage for the application of these materials in fluorescent imaging[3].

Nanogels were characterizad through DLS (Dynamic Light Scattering), TEM (Transmition Electron Microscopy), SEM (Scaning Electron Microscopy), UV-visible spectroscopy, Fluorescence spectroscopy, Individual particle fluorescence microscope, among others.

Nanogels of ~120 nm diameter of poly-HEMA were obtained by inverse mini emulsion polymerization, however an exhaustive process of dialysis is necessary to eliminate all surfactant. On the other hand, nanogels of ~150 nm diameter of poly-METAC were obtained by direct irradiation of solution containing CPNPs and monomers. All synthesized nanogels maintain intact CP properties, as confirm by spectroscopic characterization.

At the present microbiological experiments with poly-METAC nanogels are being performed to corroborate their antifouling activity.

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Multifunctional Magnetic and Photoresponsive Nanoparticles Prepared by Polymer Self-Assembly

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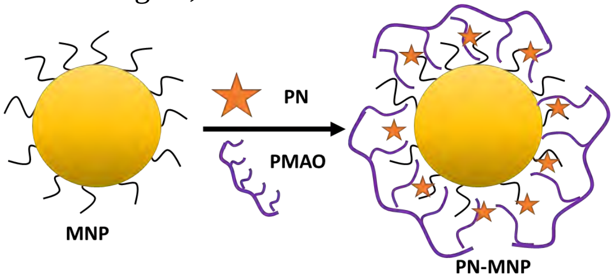
Cancer is one of the main causes of mortality around the world. One of the most sought objectives in Nanomedicine is to develop new nanomaterials that can improve the efficiency of cancer treatments while minimizing their undesired side effects. This work aims to demonstrate the synthesis of a multifunctional nanomaterial that combines magnetic nanoparticles and a photoresponsive agent in a single theranostic platform.

We synthesized monodisperse hydrophobic iron oxide nanoparticles (MNP) with a diameter of 10.8±1.5 nm by the method of Sun et al.[1]. To prepare water-dispersible nanoparticles loaded with a photoresponsive agent, the MNPs were assembled with the amphiphilic polymer poly(maleic anhydride-alt-1-octadecene) (PMAO) and dispersed in a sodium borate buffer. The hydrophobic MNPs are encapsulated by the non-polar ends of the polymer, allowing the incorporation of phenalenone (PN) as a photoactive agent, as shown in the scheme below.



By taking advantage of the magnetic properties of the nanoparticles, we employed magnetic decantation as a purification method[2] and investigated the spectroscopic properties of the precipitated and supernatant portions of the colloidal dispersion. Steady-state fluorescence spectroscopy confirmed that the photosensitizer is effectively incorporated into the assembly and revealed a photoluminescence band at $\lambda \approx 500$ nm ($\lambda_{exc}=360$ nm), which is red-shifted compared to the emission obtained for the PN in the absence of MNP.

This multifunctional nanoparticle system is a proof-of-concept demonstration of an integrated material that would allow simultaneous application of magnetic hyperthermia and photodynamic therapies. Our approach is also a promising way to deliver hydrophobic photosensitizers, as the solubilization and targeting of these molecules remains one of the biggest problems for the effective of these therapies. Finally, the use of a polymer that is sensitive to changes in temperature or pH conditions could favor the release of the photosensitizer during the combined treatment.

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Arylboron compounds as New Host-guest Dyes: Photoinduced Electron Transfer and controlled polymerization process

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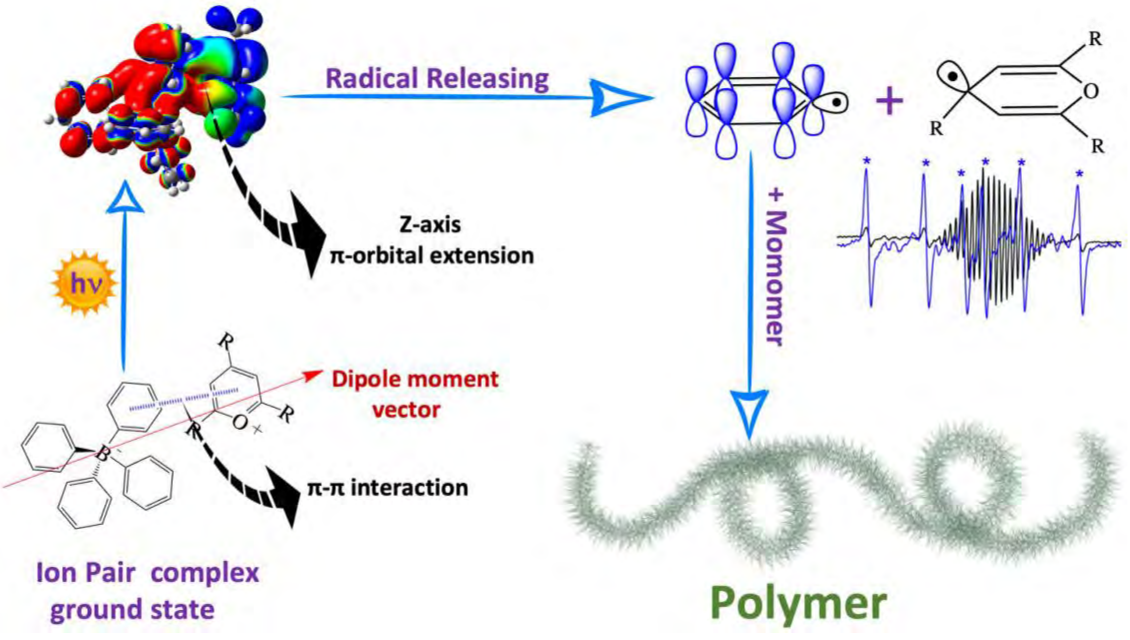
Ultrafast transient absorption spectroscopy, NOESY-NMR and EPR spectroscopy shed light how π-π stacking interactions combined with electrostatic interactions can be used to form a stable ion-pair complexes between pyrylium and tetraarylborate ions in which the interaction of the π-delocalized clouds promotes the observation of new radiative processes and also electron transfer process excitation using visible light. The results exhibit a striking combination of properties: chemical stability, photophysical and photo-chemical events that makes these ion-pair complexes as a step towards the realization of chromophore/luminescent materials and also the usage as new mono-photoinitiator system for controlled radical polymerization reactions.



Photochemical and Photophysical Studies of Biosupramolecular Complex of Toluidine Blue Derivatives and Human Serum Albumin

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Photodynamic therapy (PDT) is an emerging therapeutic treatment for cancer. PDT, which is a minimally invasive process, requires the use of a molecule called photosensitizer (PS), which contains a natural or synthetic chromophore that absorbs light of a specific wavelength. This PS is incorporated into the tumoral tissue and is then excited by a source of light to generate reactive oxygen species (ROS) that are aimed to destroy tumoral cells.[1] One of the most important challenges of this therapy is the development of new PS, that present better selectivity, and for that reason our research is focused on the use of biosupramolecular complexes as drug delivery systems.

The advantages of using proteins as carriers of different molecules are well reported in the literature. A useful protein to develop PS carriers is human serum albumin (HSA).[2] HSA has been shown to enhance the selectivity of different cancer drugs and different PS.[3,4]

In the present work, we propose to develop biosupramolecular complexes with a toluidine blue (TBO$^+$) derivative that is covalently conjugated with HAS (Figure 1). Specifically, we will present results on the photophysical properties of the complexes such as absorption and emission spectra, time-resolved fluorescence, photostability and singlet oxygen generation.

Figure 1. Derivative of Toluidine blue (TBO$^+$) that is covalently conjugated with HSA

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Poster Po38

The pyridine benzimidazole 2,4-di-tert-butyl-6-(3H-imidazo[4,5-c]pyridine-2-yl)phenol suitability for fluorescence staining in cells and antimicrobial properties.

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Benzimidazoles presenting intramolecular hydrogen bonding interactions have been normally used to better understand the role of H-bonding in biological processes. [1] The electronic and optical properties of **B2** were studied with theoretical calculations using density functional theory (DFT) and time-dependent DFT (TDDFT). **B2** showed luminescent emission at room temperature in different solvents, with a large Stokes shift (*e.g.*; λ_{ex} = 335 nm; λ_{em} = 510 nm in acetonitrile). Also, the quantum yield (φ = 0.21) and theoretical band emission are reported. [2] We observed that **B2** exerted an antifungal effect against *Cryptococcus* spp. In addition, due to its fluorescence properties, **B2** has proven to be a suitable marker to observe bacteria (*Salmonella enterica* and an *Escherichia coli* derivative) and yeasts (*Candida albicans*), both walled cell models, by confocal microscopy. Also we determined that **B2** is biocompatible by cytotoxicity experiments in HeLa cells, an epithelial cell line (non-walled cell). Fluorescence microscopy studies confirmed that **B2** accumulates in the endoplasmic reticulum (ER) and Golgi apparatus (in HeLa), two organelles involved in the secretory pathway.[3] Finally, **B2** provides a biocompatible, rapid, simple, and efficient way to fluorescently label particular organelles, producing similar results to that obtained with other well-established but more complex methods.

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Poster Po39

Magnetic and Silica Nanoparticles. Applications to Photodynamic Therapy.

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Photodynamic therapy requires the selective incorporation of the photosensitizer into tumor tissue and nanoparticles have being extensively studied for this purpose.

Magnetic nanoparticles have the great advantage of being able to target the tissue of interest with the use of external magnets. Therefore, we study them as a possible delivery system for riboflavin (RF), a photosensitizer widely studied in our laboratory. The use of magnetic materials in biological systems requires that they must be superparamagnetic, that is, they do not have magnetism in the absence of an external magnetic field. This is achieved when the size of the nanoparticle is small enough to have a single magnetic domain (tens of nm), which avoids the spontaneous aggregation of the larger magnetic particles.

A synthesis method was developed using stirring at 30,000 rpm and citric acid and oleic acid as stabilizers. Superparamagnetic nanoparticles were obtained, which were characterized by transmission electron microscopy (TEM) and were shown to be spherical, with a diameter close to 10 nm. RF was added to the reaction medium to incorporate the photosensitizer, but the RF fluorescence signal decreased dramatically when washing the nanoparticles.

The magnetic nanoparticles were coated with a silica layer with the aim to incorporate the RF into it. The silylation was performed by the reverse vesicle procedure, but again the RF fluorescence signal decreased with the washes.

To avoid the loss of the photosensitizer, RF was covalently bound to the silica. An alcohololysis reaction of the 4 OH^- groups of the RF ribityl chain was performed on isocyanate groups to incorporate 4 ethoxysilane groups into the photosensitizer ($RF(Si)_4$). The compound was characterized by IR and ^{13}C, ^{1}H, HH-COZY, ^{13}C-DEPT, HC-COZY and HMBC NMR spectroscopy and it was demonstrated that RF retained its photochemical and photophysical properties.

Silylated magnetic nanoparticles ($RF(Si)_4@Si@Fe_3O_4$) were synthesized incorporating the $RF(Si)_4$ compound and as a control Si nanoparticles were synthesized incorporating the $RF(Si)_4$ compound, ($RF(Si)_4@Si$); in both cases the RF binding was stable. The photochemical and photophysical properties of the $RF(Si)_4@Si@Fe_3O_4$, $RF(Si)_4@Si$, and of the $RF(Si)_4$ compound were studied.

The photophysical and photochemical properties of RF were retained in the $RF(Si)_4@Si$ as in $RF(Si)_4$, however, the $RF(Si)_4@Si@Fe_3O_4$ lost the photochemical properties of RF, specifically that of generating singlet oxygen, which is the fundamental property for their action as a photosensitizer.

$RF(Si)_4@Si$ nanoparticles were used as delivery system for RF on human HeLa cells (cervical cancer) and HL-60 cells (leukemia) which were irradiated with blue light. An important effect on cell viability was observed for both cell lines. The effect was maintained for much longer time than that of free RF.

Acknowledgments

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Poster Po40

Photooxidation of lysozyme sensitized by Rose Bengal: cross-linking involving tyrosine and tryptophan as markers of type 1 reactions

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This work examined the hypothesis that interactions of Rose Bengal (RB^{2-}) with lysozyme (Lyso) might mediate type 1 photoreactions resulting in protein cross-linking even under conditions favoring $^1O_2$ formation. UV-visible spectrophotometry, isothermal titration calorimetry (ITC), and docking analysis were employed to characterize RB^{2-}-Lyso interactions, while oxidation of Lyso was studied by SDS-PAGE gels, extent of amino acid consumption, and liquid chromatography (LC) with mass detection (employing tryptic peptides digested in $H_2{}^{18}O$ and H_2O). Docking studies showed five interaction sites including the active site. Hydrophobic interactions induced a red shift of the visible spectrum of RB^{2-} giving a Kd of 4.8 μM, while data from ITC studies, yielded a Kd of 0.68 μM as an average of the interactions with stoichiometry of 3.3 RB^{2-} per Lyso. LC analysis showed a high consumption of readily-oxidized amino acids (His, Trp, Met and Tyr) located at different and diverse locations within the protein. This appears to reflect extensive damage on the protein probably mediated by a type 2 ($^1O_2$) mechanism. In contrast, docking and mass spectrometry analysis provided evidence for the generation of specific intra- (Tyr23-Tyr20) and inter-molecular (Tyr23-Trp62) Lyso cross-links, and Lyso dimer formation via radical-radical, type 1 mechanisms.

Acknowledgements

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Poster Po41

Synergistic effect of Carboxipterin and Methylene blue applied to antimicrobial photodynamic therapy against mature biofilm of Klebsiella pneumoniae

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Multidrug resistance (MDR) bacteria is a serious and frequent health problem that results in the failure of infections treatment. Currently, new strategies for the control of the infections caused by these microorganisms are urgently needed. Notoriously, some MDR microorganisms generate complex structures or biofilms, which adhere to surfaces and confer extraordinary resistance properties that are fundamental challenges to control infections. One of the promising strategies for the control of MDR bacteria is antimicrobial photodynamic therapy that is a minimally invasive technique based on a photochemical process in which a non-toxic photosensitizer (PS) can be activated by low doses of radiation of a specific wavelength [1][2]. The absorbed energy generates radicals on biomolecules and highly reactive oxygen species (ROS), including superoxide anion ($O_2^{\bullet -}$) and hydroxyl radicals ($OH^{\bullet}$) (Type I reactions) or singlet oxygen ($^1O_2$, type II reactions) that cause cytotoxic damage and cell death [3]. The selection of PSs is the key point to get successful results in the aPDT treatment. Habitual PDI treatments use only methylene blue (MB, 3,7-bis (dimethylamino)-phenothiazin-5-ium chloride) that under radiation it shows bactericidal effects against both Gram-positive and Gram-negative bacteria, but MDR microorganism eradication is not completely achieved. In particular, *Klebsiella pneumoniae* is an opportunistic Gram negative pathogen, responsible of several diseases, such as urinary tract infections, pneumonia, septicemias, and soft tissue infections [4]. Some *K. pneumoniae* strains are extremely resistant to antibiotic treatments due to their capacity to generate biofilms. The key result of this study revealed that a combination of two known PSs, 6-carboxypterin (Cap, 100 µM) and methylene blue (MB, 2.5-10 µM) exposed to ultraviolet and visible radiation, presents a synergistic effect on the eradication of a MDR *Klebsiella pneumoniae* strain. Similar effect was observed when the treatment was performed either with planktonic or biofilm growing cells. Moreover, it was found that after treatment the killing action continues in the absence of irradiation leading to the eradication of the microorganisms growing in biofilm.

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Increasing the efficacy of antimicrobial photodynamic therapy with phenothiazinium dyes by controlling of aggregation

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Several compounds have been studied and their photoantimicrobial chemotherapy (PACT) action reported in the literature, specially the phenothiazinium compounds, which includes methylene blue (MB). Despite these reports on the effectiveness in fungal cells, scientific evidence shows that the medium in which antimicrobial agent is delivered may directly interfere with the efficacy of PACT due to the tendency of the antimicrobial to aggregate. Based on that, recently our research group showed that the PACT effect of MB was potentiated when using a formulation that controlled the aggregation. [1] Other phenothiazinium dyes (PD), such as Azure A (AA), Azure B (AB) and Dimethyl methylene blue (DMMB), present chemical structures similar to MB however their antimicrobial activities are less investigated. Therefore, the objective of this study was to evaluate among this series of phenothiazinium dyes if the control of aggregation can increase the effectiveness of in planktonic cells of *Candida albicans*. For this, the inoculum was treated with the compounds in different media (water, phosphate buffer saline – PBS, physiological solution – 0,9% NaCl, urea 1mol/L and sodium dodecylsulfate 0,25% - SDS) at 20mg/L for AA and AB and 0.5mg/L for DMMB. for 5 minutes in the dark, followed by exposure to 640±12 nm LED during 30 minutes, 2.6 mW/cm^2. After treatment, the diluted samples were grown on Sabouraud dextrose agar and maintained at 37 ° C for 24 hours. When used at 20mg/mL, AA and AB do not inactivate *C. albicans* in the media evaluated, except in SDS, were the inactivation was complete. DMMB cause no reduction in CFU in PBS and urea, reduced 1.0 and 1.5 Log$_{10}$ in water and NaCl respectively, while inactivated completely in SDS. Our group already reported that SDS reduces de aggregation of MB [1] and we also determined that it also reduces aggregation of PD. Here we could show that in greatly influences the PD PACT action in *C albicans* suggesting that it is important to show an suitable vehicle to administrate the photosensitizer when applying clinically PACT.

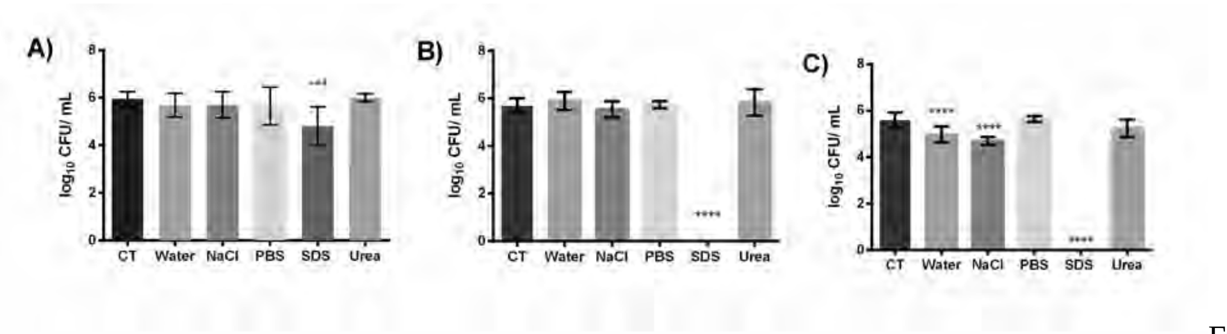

Figure1. The PACT action is dependente upon the media of photosensitizer delivery, reaching inactivation in SDS.

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Poster Po43

Photocatalytic degradation of aqueous Rhodamine 6G using supported TiO_2 catalysts. A model for the removal of organic contaminants from industrial water effluents

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As a model for the removal of complex organic contaminants from industrial water effluents, the heterogeneous photocatalytic degradation of Rhodamin 6G was studied using TiO_2 derived catalysts, incorporated in water as suspension as well as supported in raschig rings. UV and Visible light were tested for the photo-degradation process. TiO_2 catalysts were synthesized following acid and basic methodologies and compared against commercial TiO_2 catalyst samples (Degussa P25 and Anatase). The bandgap (Eg) of the TiO_2 catalysts was determined, were values of 2.97 eV and 2.98 eV were obtained for the material obtained using acid and basic conditions respectively, and 3.02 eV for Degussa P25 and 3.18 eV for anatase commercial TiO_2 samples.

Raschig rings-supported TiO_2 catalysts display a good photocatalytic performance when compared to equivalent amounts of TiO_2 in aqueous suspension, even though a large surface area of TiO_2 material is lost upon support. This is particularly evident by taking into account that the characteristics (XRD, RD, Eg) and observed photodegradative performance of the synthesized catalysts are in good agreement with the commercial TiO_2 samples, and that the RH6G photodegradation differences observed with the light sources considered are minimal in the presence of TiO_2 catalysts.

The presence of additives induce changes in the kinetics and efficiency of the TiO_2-catalyzed photodegradation of Rh6G, particularly when white light is used in the process, pointing towards a complex phenomenon, however the stability of the supported photocatalytic systems is acceptable in the presence of the studied additives. In line with this, the magnitude of the chemical oxygen demand, indicates that besides the different complex photophysical processes taking place, the endproducts of the considered photocatalytic systems appears to be similar.

3-Hydroxykynurenine bound to eye lens proteins induces oxidative modifications in crystalline proteins through a type I photosensitizing mechanism

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Photosensitized reactions mediated by endogenous chromophores have been associated with the etiology of age-related cataract disease. Endogenous chromophores such as 3-hydroxykynurenine (3OHKN) can be found in both free form, and bound to crystallin proteins. However, their efficiency in generating photo-induced oxidative modifications on eye lens proteins is not completely understood. In this work, the efficiency and photodynamic activity of 3OHKN bound to both lysine (3OHKN-Lys) and bovine lens proteins (3OHKN-BLP) was assessed and compared with the photosensitizing activity of the major chromophore arising from glucose degradation (GDC). The photosensitizing activity of 3OHKN-Lys, 3OHKN-BLP and GDC was characterized by measurement of singlet oxygen quantum yields, O_2 consumption, SDS-PAGE and amino acid analysis of the photo-oxidized proteins. Singlet oxygen quantum yields under 20% O_2 atmosphere were 0.02, 0.01, and 0.27 for 3OHKN-Lys, 3OHKN-BLP and GDC, respectively. O_2 consumption by photosensitized reactions was more efficient for 3OHKN-BLP, with the extent of O_2 consumption being ~28% higher than for 3OHKN-Lys and GDC under both 5 and 20% O_2. SDS-PAGE showed that protein crosslinking is dependent on the O_2 concentration, and more extensive at 5 than 20% O_2. GDC and 3OHKN-Lys were the most efficient crosslinkers at 20 and 5% O_2, respectively. Amino acid analysis of the irradiated proteins showed consumption of Trp, His, Tyr and Phe, and formation of kynurenine (from Trp), methionine sulfoxide (from Met) and DOPA (from Tyr). Kynurenine formation was dependent on the O_2 concentration with higher amounts detected at 5 than 20% O_2 for 3OHKN-BLP and 3OHKN-Lys, with 3OHKN-BLP the most efficient sensitizer. Our results suggest that 3OHKN-BLP can elicit photo-oxidative damage mainly by a type I photosensitizing mechanism, with this likely to be the most prevalent pathway at the low physiologic O_2 concentrations in the eye lens.

Poster Po45

Survival pathways activated in cholangiocarcinoma cells photosensitized by aluminum phthalocyanine chloride

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Photodynamic therapy (PDT) is a last-line curative treatment modality used for several types of cancer such as the cholangiocarcinoma (bile duct cancer) expecting to prolong the survival of patients. The energy fluence (dose) delivered on cells is one of the main features to induce cellular death after PDT. Thus, the understanding of the cell survival under different doses remains as key issue for applying PDT as a standard therapy. Here we hypothesized that cholangiocarcinoma cells can survive after suboptimal irradiation through activation of survival pathways. In this scenario, the cytotoxic effect of PDT was evaluated in a metastatic cell line of cholangiocarcinoma (EGI-1). Cells were photosensitized by aluminum phthalocyanine chloride into nanoemulsion (0.5 µM; 1 h) at 1, 4 and 16 J/cm^2 using a 671-nm solid-state diode laser (CNI, Changchun, China). Then, the viability was evaluated by protein content (SRB assay) and mitochondrial activity by WST-1 assay, reactive oxygen species (ROS) generation detected by DCFH$_2$-DA probe, cell growth by clonogenicity, DNA cell cycle and apoptosis detected by flow cytometry in different times (1.5 to 6 h after PDT). Image visualization of cell death kinetics were also obtained by the IncuCyte$^{®}$ S3 Live-Cell Analysis System. Finally, RNA-Seq transcriptome analysis was performed to detect survival pathways triggered by PDT. In general, PDT induced EGI-1 cell death activation as a dose-dependent effect, at 16 J/cm^2 a significant ($p<0.05$) reduction in total protein content (64% cell density) in the first 2 h post-PDT was detected, and metabolic activity decreased ($p <0.05$) to 7% at this dose. Apoptosis (annexin V-positive cells) appears as the preferential mechanism triggered after cytotoxic stress induced by PDT combined to a massive formation of apoptotic bodies. A fast ROS bursting immediately (10 min) to PDT procedure corresponding to 2.1-fold change ($p<0.05$) at 16 J/cm^2 is pointed out as the mechanism of action culminating in cytotoxicity. Cell survival analyses figured out that only mildly injured cells at 1 J/cm^2 can proliferate in long-term, where the PDT-effect on metabolism, protein content, ROS generated are minimally detected in short-time post-PDT. In this condition, cells activated survival mainly by induced unfolded protein response (UPR). The UPR is a process that is initiated upon endoplasmic reticulum stress. By UPR, unfolded and misfolded proteins are degraded, and molecular players involved in protein folding are upregulated. However, apoptotic cell death is triggered when the amount of damaged proteins exceeds a certain threshold, which can occur at 4 and 16 J/cm^2. Thus, PDT on cholangiocarcinoma cells leads to cell death induction, mainly by apoptosis, at high energy fluences. However, these cells kept proliferative functions close to normal level when low energy fluence was used. This event remains as an obstacle to an effective PDT, since the energy fluence can be modulated by the scattering of light through tissue deepness.

Effects of inclusion complex of β-Cyclodextrin and Hypericin in photodynamic therapy

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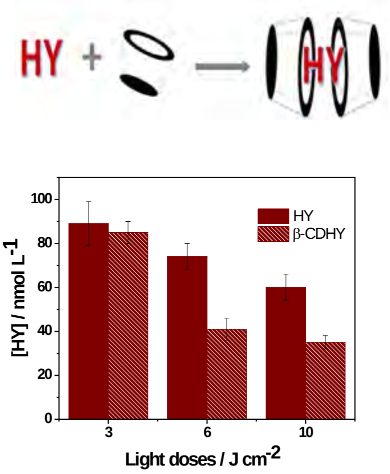
Photodynamic Therapy (PDT) is founded on the administration of a non-toxic compound called photosensitizer (PS) followed by visible light irradiation at a suitable wavelength leading to reactive oxygen species which induces oxygen death of the target cells. Hypericin (HY) is a PS largely used in PDT of cancer. However, HY is poorly soluble in an aqueous medium, which restrains its bioavailability and decreases its PDT efficiency. β-Cyclodextrin is a type of cyclic oligosaccharide that has seven glucopyranose units, forming a hydrophobic internal cavity and a hydrophilic external surface which allows host-guest complexes formation with other molecules, essentially hydrophobic. Despite cyclodextrins are largely used as a carrier system, there are no reported studies about these host-guest complexes with HY for PDT uses. For this reason, in this study host-guest complex between HY and β-CD, named as β-CDHY, was synthesized by the co-solvent method with sonication. The evidence of complex formation was given by infrared spectroscopy and NMR-^{1}H. The molar proportion of the complexation was 1:2 (HY: β-CD), suggesting the structure represented in the figure. A complexation efficiency of 42% was obtained and HY became soluble after complexation. The release profile showed an increase of almost five times in the β-CDHY release compared to free HY. No changes in photostability and fluorescence quantum yield were observed. However, cell uptake and phototoxicity of the complex were evaluated by the first time in tumor cells (HeLa) after 2 h of incubation and it was noticed a twofold increase in cellular uptake and an improvement of 40% in phototoxicity after irradiation with a 590 ± 10 nm LED with three light doses: 3, 6 and 10 J cm^{-2} and 8.4 mW cm^{-2}, as it is showed in Fig. 1. The rise in phototoxicity can be justified by the increase of water solubility of HY after the host-guest complex formation, which consequently enhances its diffusion in physiologic medium, improving the cell accumulation. These advantages suggest that β-CDHY has a potential for use in PDT.

Fig.1*: Struture of β-CDHY and IC50 in HeLa cells of three and complexed HY in three different light doses.*



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Key words: Hypericin; β-Cyclodextrin; Photodynamic Therapy

Poster Po47

Media for photosensitizer delivery affects aggregation and generation of reactive oxygen species of phenothiazinium dyes

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In Photodynamic therapy (PDT), the therapeutic aid based in the use of a photosensitizer (PS) associated with light and the cell death is triggered by the production of reactive oxygen species (ROS), among them, singlet oxygen ($^1O_2$). Methylene blue (MB) is a phenothiazinium dye that have been studied in several PDT works, mainly due to its high absorption of light in the region between 550-700 nm and low cost, however, it is known that due to aggregation, the production of $^1O_2$ may be compromised depending upon the medium used [1]. Other phenothiazinium such as Azure A (AA), Azure B (AB) and dimethyl methylene blue (DMMB) may also present similar behavior. Thus, the objective of this study was to evaluate the aggregation of this series of compounds and measure the production of ROS in different media (water, phosphate buffer saline – PBS, physiological solution – 0,9% NaCl, urea 1mol/L and sodium dodecylsulfate 0,25% - SDS). The aggregation of the PSs was determined by spectrophotometry, by the calculation of the dimer-monomer ratios (D/M: employing the absorbance values for the dimer and monomer of each compound, respectively). The production of ROS was measured using the p-Nitrosodimethylaniline (RNO) [2]. The aggregation tendency observed was smaller for MB, higher for DMMB and intermediate for AB and AA, being slightly bigger for AA. Because they are more hydrophilic, the changes in D/M values of MB, AA and AB between the media is not very high. On the other hand, for the DMMB it is possible to observe the significant changes in the D/M in the different media, being lower in SDS, slightly higher in urea; in water the D/M value is intermediate, increasing in PBS and reaching the maximum in physiological solution. The ROS production increased depending upon the media used, being lower in urea, followed by PBS, NaCl, SDS and it was higher in water. The ROS production measured by RNO showed no relation to aggregation, suggesting that the oxidant species measured were produced by type I reaction. Some studies show that RNO measures production of hydroxyl radicals ($^{\bullet}OH$), since it do not react with $^1O_2$ and superoxide. Thus, the production of $^{\bullet}OH$ is similar between the compounds, and depends on the media used to deliver the PS. In SDS the $^{\bullet}OH$ production differs between the compounds, being greater for DMMB.

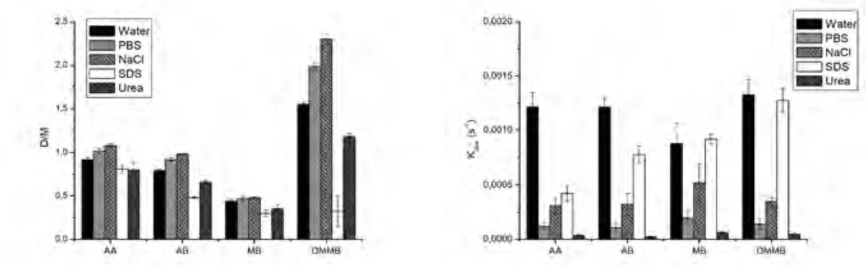

Figure1. Dimer to monomer ratio and rate constants of $^{\bullet}OH$ production by RNO method.

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Photoactive dye doped polymeric nanoparticles: an efficient toolbox in photodynamic inactivation of pathogens

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Microorganisms, particularly bacteria, have been natives of the earth for 3.5 millions of years and their evolution demonstrates that they can adapt to many different environments. The antibiotic development has seemed to give battle against pathogens. However, in 2017 the World Health Organization (WHO) published its first-ever list of antibiotic-resistant priority pathogens. The most critical group of multidrug resistant bacteria were *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae,* and the methicillin-resistant *Staphylococcus aureus* (MRSA). In response to this latent threat, scientists developed alternative therapies such as photodynamic inactivation (PDI), which emerged late in the 20th century as a promising treatment to kill pathogens. In this work, we efficiently combine photoactive dye doped polymeric nanoparticles (NPs) with blue light to kill some multidrug pathogens included in the WHO list. Initial screening with different NPs concentrations (0.3 to 6.5 ppm) and irradiation doses was performed in nine pathogenic strains to explore the efficiency of the PDI treatment in planktonic cells. Bactericidal effect was observed in MRSA strains using short irradiation period/ low light dose (10-15 min/ 24-36 J/cm^2). The Gram-negative species required higher light (72 J/cm^2) and NPs (16.5 ppm) doses. Bacterial NPs uptake was initially studied using bright-field and fluorescent microscopy taking advantage of the intrinsic NPs fluorescence. Further studies on NPs uptake for different bacterial species were performed using flow cytometry. Restults from both techniques indicate that NPs superficially bind and slightly penetrate the bacterial envelope. To further explore PDI treatment strategies using our NPs we tested their performance on mature bacterial biofilms. In both Gram-positive and negative bacteria, the crystal violet assay displayed a similar antibiofilm trend after PDI treatment. At the same time, the effect achieved on the metabolic activity of the cellular cluster after PDI treatment was larger in Gram-negative cells than Gram-positive strains; showing a drop in the activity between 67 to 84 % respect to the control. To further test the overall effect on the biofilm matrix and the eradication effect of our PDI therapy we used confocal microscopy. For these experiments *E. coli* and *S. aureus* were selected and both strains exhibited substantial matrix disruption. Notably, almost complete biofilm eradication was achieved for the *E. coli* strain. Overall, our results demonstrated that PDI protocols using NPs plus blue light are an efficient tool not only to kill superbugs as sessile cells but also to disrupt and eradicate mature biofilms of relevant bacterial species.

Poster Po49

Upconversion nanoparticles for Energy and Biomedicine applications

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Lanthanides compounds have been widely used in energy conversion processes (down-shifting, down-conversion and up-conversion). In particular, upconversion nanoparticles (UCNP) have been used since the 60's of the last century in several different applications. Infrared pumping and emission spanning the UV-Vis region up to the infrared is very attractive from the technological point of view. In this presentation we will show 3 may examples where light activated processes like photodynamic therapy, photocatalysis and temperature measurements can benefit from the spectral properties of UCNP [1-3] modified at the surface sílica and titânia through sol-gel methods.

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Poster Po50

UV-light induced conformational changes in β-lactoglobulin improves digestibility and generation of bioactive peptides

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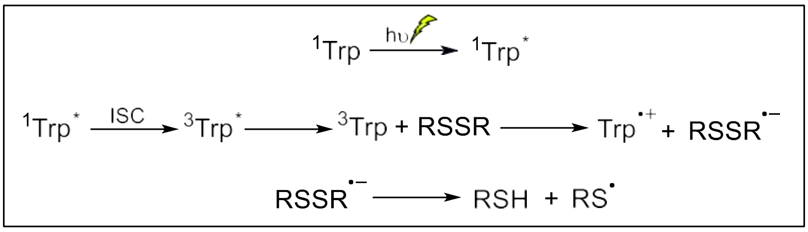
β-lactoglobulin (β-lg) is the main protein in whey and accounts for about 10% of the total milk proteins. β-lg is a globular protein (18.3 kDa) with two disulfide bridges ($Cys_{160}Cys_{66}$ and $Cys_{106}Cys_{119}$) and one free thiol group (Cys_{121}). In its native state, β-lg has predominant β-sheet structure and in natural pH found as a dimer in solution. In acidic medium, β-lg is predominantly found as a monomer retaining its globular structure which gives a high stability to digestion by the gastrointestinal tract. Due to its high stability to digestion, β-lg is found as an important allergen in cow's milk allergy. UV-C light processing in food industry is an emerging non-thermal technology for microbial inactivation and its effects in the major food constituents are scarce. In this view we report herein the effects of UV-C light processing in the structure and resistance to digestion of β-lg. After UV-C photolysis (λ = 266 nm; light intensity = 0.0015±0.0003, β-lg was found a slightly change in the secondary structure: increase in β-sheet structure front 47% (native) to 52% (photolyzed) with reduction of randomic, α-helix and β-turn contribution. This change, retaining the globular structure, were induced by the cleavage of the RSSR bridges as promoted by UV-C light with an $\Phi = 1.96\text{x}10^{-10}$ E s^{-1} (80 W m^{2}). The resistance to digestion was significantly affected, and β-lg irradiated was found to be around 200% more digested in a simulated gastric fluid in comparison to native β-lg. Transient absorption of laser flash photolysis showed that the main photochemical process which accounts to β-lg modification is induced by cleavage of RSSR bounds mediated by triplet-excited tryptophan (Trp) in close vicinity according to:



$$^{1}\text{Trp} \xrightarrow{h\nu} {}^{1}\text{Trp}^{*}$$

$$^{1}\text{Trp}^{*} \xrightarrow{\text{ISC}} {}^{3}\text{Trp}^{*} \longrightarrow {}^{3}\text{Trp} + \text{RSSR} \longrightarrow \text{Trp}^{\bullet+} + \text{RSSR}^{\bullet-}$$

$$\text{RSSR}^{\bullet-} \longrightarrow \text{RSH} + \text{RS}^{\bullet}$$

In addition to the reduced resistance to digestion in the simulated gastric fluid, the released peptide profile was found to be affected and β-lg irradiated showed the potential to release bioactive peptides during digestion. In conclusion, UV light showed to be a promising non-thermal processing technology to reduce β-lg resistance to digestion and allergenicity, at the same time maintain the protein globular structure in solution.

Acknowledgement

FAPESP (2017/01189-0), CNPq (306491/2015-0) and CAPES (CODE 001) for the financial support.

Derivado Trifenilfosfonio de Furilvinilnaftoxazol. Sensor fluorescente de Oxígeno Singulete en Células

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El oxígeno molecular singlete (O_2 ($^1\Delta_g$), en lo sucesivo $^1O_2$), el primer estado electrónico excitado de la molécula de oxígeno, es una especie de oxígeno altamente reactiva (ROS) capaz de oxidar componentes celulares ricos en electrones como proteínas, ácidos nucleicos y estructuras lipídicas. El $^1O_2$ juega un papel clave en una amplia variedad de procesos químicos y biológicos, entre otros, en síntesis orgánica, terapia fotodinámica del cáncer, erradicación de microorganismos patógenos, o señalización celular. A pesar de su relevancia, solo hay algunas técnicas disponibles para monitorear el $^1O_2$ en medios biológicos. La técnica preferente es la detección óptica de su fosforescencia en el infrarrojo cercano a 1270 nm. Sin embargo, la detección de fosforescencia NIR requiere un equipo sofisticado disponible solo en unos pocos laboratorios especializados y además, la detección de un número reducido de fotones plantea sustantivos desafíos técnicos. No es sorprendente que se hayan desarrollado métodos de detección alternativos más simples pero indirectos basados en sondas que reaccionan selectivamente con $^1O_2$. Entre ellos, las sondas fluorescentes son herramientas atractivas para la detección de $^1O_2$ en medios biológicos debido a su alta sensibilidad y respuesta rápida, junto con la adopción generalizada de microscopía de fluorescencia y técnicas de imagen.
En nuestro laboratorio se han desarrollado sondas fluorescentes del tipo "apagado encendido", exitosas para la detección de oxígeno singulete.[1] Estas sondas furil derivados del vinilnaftoxazol (FN), muestran un notable aumento de la fluorescencia del grupo naftoxazol luego de la reacción del residuo furano con $^1O_2$. Sin embargo, uno de los desafíos a abordar, es el aumento de la capacidad de penetración de la sonda en celulas, lo que permitiría su uso en estos sistemas.

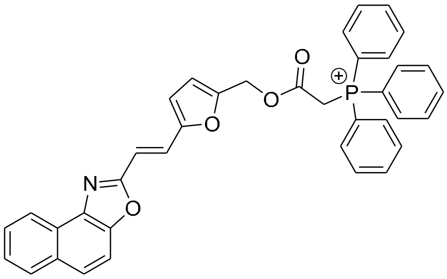

Figura 1. Estructura molecular de (E)-(2-((5-(2-(nafto[1,2-d]oxazol-2-il)vinil)furan-2-il)metoxi)-2-oxoetil)trifenilfosfonio

En este trabajo, se reportan los resultados relativos a la síntesis y los estudios fotoquímicos y fotofísicos observados en medio homogéneo y en celulas con la sonda (E)-(2-((5-(2-(nafto[1,2-d]oxazol-2-il)vinil)furan-2-il)metoxi)-2-oxoetil)trifenilfosfonio (Figura 1), que incluye un grupo trifenilfosfonio terminal, conocido orientador mitocondrial.

Los autores agradecen el financiamiento de FONDECYT, Proyecto 1150210.

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Chitosan-Photosensitizer Conjugate: Photophysical Characterization and Antifungal Photodynamic Therapy application on two fruit Pathogenic Fungi.

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Pathogenic Fungi presence in plants and fruits are an alarming problem and causes production losses in the agricultural industry reaching 50% of production losses in developing countries. The use of traditional fungicides partially solves this problem but leaves serious consequences such as harmful residues on fruits, environmental contamination and the apparition of resistant fungal strains. A promising alternative to traditional fungicides is using Antimicrobial Photodynamic Therapy (aPDT) as a platform to develop brand new fungicidal formulations based on the cytotoxic effect of reactive oxygen species (ROS), specifically Singlet Oxygen ($^1O_2$) generated by a photosensitizer (PS) and the irradiation of light. The results reported in the literature indicate that aPDT effectively has fungicidal activity in different strains of fungi. Another alternative to traditional fungicides is Chitosan (CH). This polymer is obtained by a deacetylation process of chitin obtained from crabs and shrimps shells is widely used as a fungicide in the agricultural industry due to its low price, biodegradability and non-toxic to the human consumption[1]. There is evidence in the literature that support the idea of using CH and PS together in aPDT. Examples are Rose Bengal and a Chitosan polycationic derivative covalent conjugate against *E. faecalis* and *P. aeruginosa* Bacteria[2] and Chlorophyllin-Chitosan physical blend against *L. monocytogenes* Bacteria[3], both researches concludes that the addition of Chitosan to the formulation enhances in some extent the photodynamic cytotoxic activity of the photosensitizer. Under this context, we propose using both aPDT and CH as a fungicide formulation through the synthesis of covalent conjugate between low molecular weight chitosan (CH_H) a PS. Specifically, Photophysics properties such as Fluorescence and Absorption Spectra, Time-Resolved Fluorescence and Anisotropy were studied as well as Photochemical processes such as Singlet Oxygen generation. Results between PS and CH_H-PS were compared. Finally, to confirm the photodynamic antifungal activity of the formulations, in vitro analysis was made against *Penicillium Digitatum* and *Botrytis Cinerea* using PS, CH_H and CH_H-PS as fungicide agents through Fungal radial growth measurements among others.

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Poster Po53

Spin Conservation in Photo-Induced Electron Transfer to Spin-Coupled Acceptors

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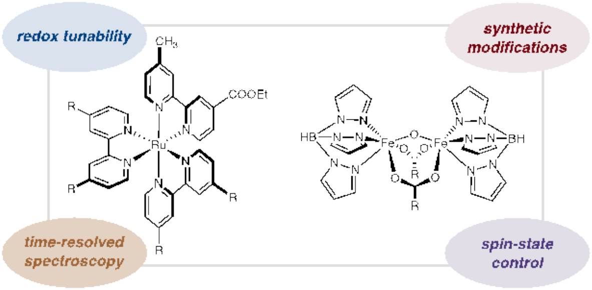
The notion of spin conservation is present in many aspects of scientific research; for example, it is commonly invoked when interpreting optical spectra. However, the effect of spin conservation on chemical reactions has received far less attention so far. Our group has previously shown that the spin of a system can drastically affect its ability to engage in energy transfer.[1]

To complement our previous research, we have focused on the effect of spin conservation on electron transfer reactions. To this end, we have combined Ru(II) polypyridyl donors with μ-oxo μ-carboxylatodiiron(III) core acceptors. The strength of spin coupling within these acceptors can be modified by protonating the oxo bridging group. In this way, we have used Heisenberg spin exchange to alter the spin states available to the diferric cores without changing their composition and/or structural properties. To study the reactivity of these systems, we have employed a variety of physical and spectroscopical techniques, including time-resolved emission and absorption.

We have observed that the rate of bimolecular electron transfer is inversely correlated to the strength of the coupling between the Fe(III) centers. These results agree with the work of Bominaar and co-workers,[2] whose theoretical analysis predicted that excited spin states may be involved in electron transfer from a spin-coupled donor to a diamagnetic acceptor. In this way, a spin-coupled metal cluster could act as a molecular switch: This could help understand how metalloproteins work, and also have applications in molecular electronics.



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Poster Po54

Determination of association constants from single molecule fluorescence microscopy

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Single molecule fluorescence microscopy can yield molecular resolution with a location precision in the tens of nanometer range in the plane perpendicular to the light propagation. This opens the possibility to count molecules and correlate their locations, starting from a map of the actual positions in a single molecule super resolution image. In this work we will present results of three experiments aiming at the calibration and determination of association constants.

The first experiment uses complementary oligonucleotides, one strand marked with Atto-565 and the other with AlexaFluor647. Hybridization is controlled by the amount of each strand and measured in steady state emission. Samples are spread on a coverslip and molecules of each type are counted on the microscope by Stochastic Optical Reconstruction Microscopy experiments with split field simultaneous two color detection. Actual distributions are compared to random ones to evaluate the association fraction and compare it with the values obtained in the correspondent bulk experiment.

In the second type of experiments we evaluate the dimerization of protein PDK1 under the presence of different aggregation inhibitors, to test their efficacy. The protein was marked with SNAP-silicon-rhodamine and the fraction of dimers was estimated by the distribution of emission intensity of the bright spots obtained in single molecule fluorescence images.

The third type of experiments was directed to establish the interaction mechanisms between three proteins that are relevant in the hypoxia adaptation of cancer cells: HIF (Hypoxia inducible factor), VHL (von Hippel-Lindau complex), RSUME (RWD-domain-containing sumoylation enhancer). These proteins were marked pairwise with SNAP-silicon-rhodamine and CLIP-tetramethylrhodamine. Their association is evaluated as a function of time in COS-7 cell lines by two color simultaneous STORM experiments. In all cases the random distribution is used as a reference for the pair correlation of locations. We present preliminary results from this strategy.

Photophysical Characterization of an Anthracene Analogous of Laurdan and Application in Microscopy.

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According Weber's definition, for an hydrophobic fluorescent probes to be used as an environmentally sensitive sensor, it must have in its structure two different substituents, having electron acceptor an donnor character respectivelly., both attached to an aromatic ring.[1] The magnitude of the sensitive response would directly depend on the separation between both substituent groups. The series of polarity sensitive fluorescent probes designed and synthesized by Weber et al, in the eighties, correspond to a naphthalene aromatic moiety, substituted with a dimethyl amino group in position two (donor group) and an alkyl carbonyl group in position 6 (acceptor group). Members of this series of compounds are PRODAN and LAURDAN among others. LAURDAN has been used in several studies involving lipids in vitro, in vivo, in cubette an microscope studies, among them we can mention: characterization of lipid phases in membranes, determination of partition coefficients, observation of shape changes during phase transition, observation of lipid-protein interactions, discrimination of cholesterol content in living cells.

To maintain the environmental sensitivity of LAURDAN but modifying the absorption spectra with a bathochromic shift, we have replaced napthalic group for anthracene group, increasing the possibility of aromatic delocalization.[2]

The photophysical behaviour of Capyrdaa in homogeneous media shows dependence with the solvent. The batochromic shift of emission spectra is observed with increase in solvent polarity. Moreover, decrease in fluorescence quatum yield with solvent polarity is also observed. However, not significant changes are observed in absorbance and lifetime with solvent.

Fluorescence microscopy determinations (mono and biphotonic) in synthetic microheterogeneous systems and cells, shohw that Caprydaa behaves as a good probe.

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Poster Po56

Oxidation mechanism of coumarin-oligopeptides derivatives promoted by electron transfer processes.

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The generation of Free radical cation species by laser irradiation of 7-aminocoumarins have allowed us developing attractive methodologies to generate free radicals in specific sites for studying oxidation and electron transfer processes in complex biological systems such as peptides or proteins.

First, we studied the dynamics and photophysics of synthesized C_{314} derivatives (Cx) linked to oligopeptides: Cx-Tyr-Trp-Arg-Arg (1), Cx-Tyr-Gly-Trp-Arg-Arg (2), Cx-Tyr-Pro-Trp-Arg-Arg (3) and Cx-Tyr-Aib-Trp-Arg-Arg (4), which were synthesized through Fmoc-based solid phase synthesis. These peptides include different spacer residues between Tyr and Trp, which modifying the rigidity/flexibility of the backbone allowing us to modulate the electron transfer processes involved in the radical migration mechanism. Specifically, it was found that an efficient static quenching mechanism of C_{314} fluorescence elicited by Trp is due to a π-stacking intramolecular interactions. This was evaluated by fluorescence quantum yields and fluorescence lifetimes that included chaotropic agents. Moreover, conformational studies of these peptides using molecular dynamics, pointing out that the spacer residue between Tyr and Trp plays a key role on the conformational dynamics of the peptides, determining the preferential conformation adopted for each peptide. To evaluate the electron transfer process from amino acids to coumarin free radical involved into peptide oxidation, laser flash photolysis technique and oxidation products analysis were carried out. The analysis of oxidation products of these peptides showed the Tyr residue is oxidized in all peptides, being a Trp-radical the principal intermediate and their formation were strongly dependent on the conformational dynamics of each peptide as is shown in the following mechanism:

$$\begin{array}{ll}
(\boldsymbol{Eq.1}) & \boldsymbol{C - YXWRR + h\nu \longrightarrow C^{*} - YXWRR} \\
(\boldsymbol{Eq.2}) & \boldsymbol{C^{*} - YXWRR + h\nu \longrightarrow C^{\bullet +} - YXWRR + e^{-}} \\
(\boldsymbol{Eq.3}) & \boldsymbol{C^{\bullet +}YXWRR \longrightarrow CYXW^{\bullet +}RR} \\
(\boldsymbol{Eq.4}) & \boldsymbol{CYXW^{\bullet +}RR \longrightarrow CY^{\bullet +}XWRR}
\end{array}$$

Moreover, an additional product corresponding to a coumarin-released peptide was found in all cases. This is directly related with the electron transfer process to the coumarin radical from Tyr.

Acknowledgment: The financial support from FONDECYT project 1190881, CONICYT FONDEQUIP UHPLC, MS/MS EQM 120065 is greatly appreciated. CONICYT PhD fellowships are gratefully acknowledged by PB (21160605).

Poster Po57

Antiparasitic photodynamic therapy against *Leishmania amazonensis* mediated by ruthenium and porphyrin photosensitizers

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Photodynamic therapy (PDT) consists on a technique in which occur a photosensitizer (PS) administration in the presence of oxygen and light in order to generate reactive oxygen species (ROS) like singlet oxygen ($^1O_2$) and hydroxyl radical ($OH^{\cdot}$). PDT has been widely used in several areas such as cancer, microorganism infections, hyperbilirubinemia, among others, as an alternative to conventional therapies to obtain an effective treatment with less toxicity. In the case of microorganism infections, leishmaniasis are neglected and incapacitating diseases, responsible for lead to death thousands of people worldwide and caused by a parasite of the *Leishmania* spp. species. The treatments for these diseases is ineffective, highly costly and toxic. For this reason, PDT studies are being performed in a variety of *Leishmania* spp. species with the goal of finding an effective, affordable and easily accessible therapy. Based on increase PDT effectiveness, some studies used compounds derived of ruthenium complexes that promote dual activity, as generators of reactive oxygen species and photoreleases drugs of interest. The main efficiency of this compounds is deliver drugs in a specific target causing less cytotoxicity and improving the effectiveness of the treatment. The studies presented promising results in the treatment of cancer cells, since they used metal based complexes that release drugs of interest upon light irradiation. Still relying on compounds used on cancer therapy, some porphyrins derivatives were studied and showing to be excellent compounds for PDT against HaCaT and HeLa cells. In this study was possible to see some difference on death mechanisms it is dependent on the compound charge. In this case, according to the positive or negative charge of the porphyrins the compounds could act on mitochondria or lysosome and generate necrosis or autophagy process. Another study was made using porphyrins derivatives as PS in the *Leishmania* ssp. parasites but almost nothing is known about death mechanism of *Leishmania* ssp. with porphyrins as PSs. So, in this work we are studying the effects of PDT on *Leishmania amazonensis*, using ruthenium complexes and porphyrin derivatives as PSs. Before understand of the death mechanism, it's important to understand the internalization of these PSs on the parasitic cell, once is described in the literature that *Leishmania* spp. has a negative membrane surface. For this reason, we studied the difference between charged compounds (positive and negative), like porphyrins, and compounds with different sizes and binders (substituents groups coordinated with metal ion). In the uptake investigations we observed that none of the studied compounds (two porphyrins derivatives: meso-cis-di-(N- methyl-4-pyridyl) diphenyl porphyrin dichloride and meso-tetraphenylporphiryn disulphonic acid disodium; and two ruthenium complexes: $[Ru(dqpy)(dppn)(5CNU)][PF_6]_2$ and $[Ru(dqpy)(phen)(5CNU)][PF_6]_2$) were dependent of concentration or time. All the compounds independent of charge and size entered the parasitic cells after 1h of incubation and kept up inside the cell about 30-40% of the initial concentration (5, 50 and 100 μM). More studies will be conducted to better understand the localization of these compounds and the type of cellular damage.

Acinetobacter nosocomialis harbors BLUF photoreceptors functional at moderate temperatures such as 37ºC

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Microorganisms from the genus *Acinetobacter* harbor from one up to six copies of Blue light using FAD (BLUF) photoreceptors in their genomes. While in *A. baumanii* photoregulation of motility is lost at temperatures ≥ 24ºC, in *A. nosocomialis* still shows photoregulation even at 37ºC. The first difference between both species is the presence of three BLUF domain-containing proteins in *A. nosocomialis*, while only one is present in *A. baumannii*, which is the well-characterized photoreceptor BlsA. Recently, we have been shown that BlsA from *A. baumanni* is temperature sensitive showing little or no photoactivity above 26ºC, which correlates well with its expression levels and BlsA protein presence in the cells.

In contrast, given that *A. nosocomialis* harbors three BLUF genes encoded in its genome, with a different photoregulation pattern as a function of temperature, we hypothesized that differential behavior of the encoded photoreceptors could account for the extended photoregulation observed at higher temperatures.To confirm this hypothesis, we have performed a biophysical and photophysical characterization of two of them. For this purpose, the open reading frames encoding for *A. nosocomialis* BLUF46 and BLUF65 were cloned into pBluescript and then transferred into pET28. The corresponding recombinant proteins were expressed and purified. In both cases, these photoreceptors have shown to have an extended range of temperature at which they are active in comparison to BlsA. BLUF46 has an active photocycle up to 32ºC while BLUF65 reaches 37ºC completely active, and thus could be responsible for the photoregulation of motility observed in *A. nosocomialis* at 37ºC. Interestingly, BLUF65 shows photophysical distinctive characteristics than is *A. baumannii* ortholog, BlsA, suggesting that differences contained in the primary structure may account for the differential temperature dependence.

Kinetic and Mechanism of the Photochemistry of Rhenium Tricarbonyl Complexes: Dependence on the P,N-bidentate Ligand Nature.

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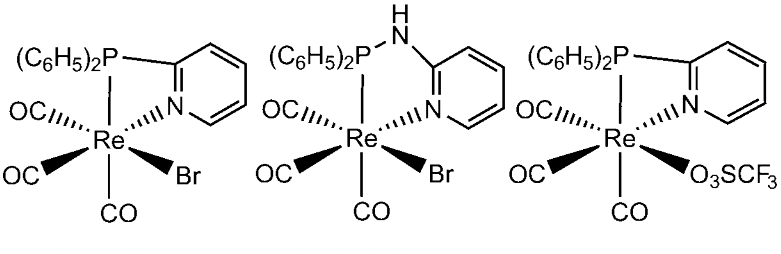
A great amount of research related to Re^{I}-diimine complexes has been developed during the last decade, however the photoproduct or reactive species generation, remain mostly unexplored, which could have potential use in practical applications such as synthesis, remediation or photodynamic therapy (PDT). Rhenium(I) complexes with hybrid *P,N*-bidentate ligands, like 2-pyridyl-diphenylphosphine, have been prepared for synthetic or catalytic purposes. We have recently reported the syntheses and photophysical properties of rhenium(I) tricarbonyl complexes with a phosphine-imine ligand: [*P,N*-$\{(C_6H_5)_2(C_5H_4N)P\}Re(CO)_3Br$] (**RePNBr**), [*P,N*-$\{(C_6H_5)_2(C_5H_4N)P\}Re(CO)_3$(*O*-$CF_3SO_3$)] (**RePNTfO**) and [*P,N*-$\{(C_6H_5)_2(C_5H_4N)NHP\}Re(CO)_3Br$] (**RePNNBr**) (Figure 1).[1-2] In this work, we present the kinetic and the photochemistry of these mononuclear complexes followed by UV-Vis at different temperatures, exploring the mechanism and the possibility of singlet oxygen, $O_2(^1\Delta_g)$, or carbon monoxide (CO) generation.



RePNBr **RePNNBr** **RePNTfO**

Fig 1. Structure of the studied complexes.

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Natural anthraquinones-mediated photodynamic inactivation: preliminary results against *Leishmania amazonensis*-induced cutaneous leishmaniasis in mice

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Cutaneous Leishmaniosis (CL) is one of the 17 neglected tropical disease classified by World Health Organization produced by *Leishmania* parasites. Following a sandfly bite in exposed areas of skin, a pink papule progresses to a nodule or plaque and eventually forms an ulcer with raised borders. So far, there is no effective treatment without toxicity and resistance.[1] Photodynamic inactivation (PDI) appears as a promising topical treatment to overcome this serious health problem. This therapy combines photosensitizers, as natural anthraquinones (AQs), and proper light to produce reactive oxygen species and kill *Leishmania* parasites.[2] A recent *in vitro* study demonstrated that Soranjidiol (Sor), Bisoranjidiol (Bisor) and 5-Chlorosoranjidiol (5-Clsor) irradiated with LED at 20 J/cm^2, reduced above 90% the promastigote viability of *Leishmania amazonensis*.[3] The aim of this work was to conduct a pilot study on infected mice to verify the effect of AQs-mediated PDI on CL.

Twelve Balb/C mice were infected in the left footpad with a suspension of $1x10^6$ promastigotes/ml and randomly divided into four groups: control (without treatment), G1 (Sor and blue LED, 410 ± 10 nm), G2 (Bisor and blue LED) and G3 (5-Clsor and green LED, 520 ± 10 nm). All AQs were assayed at 10 μM and LEDs were set to deliver a fluence of 45 J/cm^2 (15 min). After treatment, parasite burden was determined by bioluminescence every day for 72 h and evolution of lesion and pain was followed during a month, measuring once a week.

Results showed that treatment with AQs tend to maintain parasite burden for 48 h after PDI, whereas 72 h post PDI, only 5-Clsor continue keeping low levels of parasite burden. Regarding lesion size and pain, no statistically significant differences were noticed among groups. However, one week after PDI, only the group treated with Sor has no ulceration on the lesion.

In conclusion, our results suggest that Sor is the most promising AQ to pursue the best protocol to treat cutaneous leishmaniasis, since it not only maintained the parasite burden for 48 h after PDI, but it also prevented ulceration in the lesion one week after PDI.

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Photodynamic inactivation of *Candida tropicalis* biofilms by parietin, a natural dihydroxyanthraquinone

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The 1,8-dihydroxy-3-methoxy-6-methylanthraquinone (Parietin, PTN), a blue-light absorbing pigment present in several lichens of the genus *Teloschistes* spp., shows photosensitizing properties through both Type I (superoxide anion, $O_2^{\bullet-}$) and Type II (singlet molecular oxygen, $^1O_2$) mechanism, with antibacterial effects *in vitro* when it was photo-stimulated [1]. The aim of this work was to evaluate the *in vitro* antifungal activity of PTN, analyzing whether this effect could be increased by actinic irradiation, and establishing if the photoinactivation mechanism involves the production of Reactive Oxygen Species (ROS).

PTN was isolated from the lichen *Teoloschistes nodulifer* (Nyl.) Hillman (*Teloschistaceae*) and it was purified by recrystallization from the acetone extract, and its purity was determined by HPLC. Minimum Inhibitory Concentration (MIC) of PTN was determined by following the protocols of the Clinical and Laboratory Standards Institute [2], testing twelve concentrations (0.24 to 500 µg/mL) in planktonic cultures of *Candida tropicalis* NCPF 3111 (10^3 cells/mL). PTN aqueous solution (ethanol as co-solvent <1%) was added to the fungal suspension following the additive serial double dilutions method, and immediately the assay was performed simultaneously under darkness and illumination during 15 min with a Philips TL/03 actinic lamp emitting in the range 380-480 nm. Under darkness, PTN did not decrease meaningfully the growth of planktonic cells of *C. tropicalis*, but under irradiation the MIC was 0.98 µg/mL.

The antifungal activity of PTN was also tested on *C. tropicalis* biofilms at three concentrations in triplicate: MIC, MIC/2 and MICx2, under darkness and same irradiation conditions than in the case of yeast suspensions. After 48 h of incubation, aliquots of biofilm were removed and serially diluted. The number of viable yeasts was determined also in triplicate, and the counting of colony forming units (CFU/mL) was log-transformed. In addition, the scavenging effect of 200 mM sodium azide ($^1O_2$ quencher) or Tiron ($O_2^{\bullet-}$ quencher) on biofilm photoinactivation by PTN was evaluated. Results show that PTN did not produced antibiofilm activity in darkness, but under blue light a 3 log reduction of the CFU at the MIC×2 was observed. Moreover, the antibiofilm photodynamic activity of PTN was completely suppressed in the presence of sodium azide or Tiron. In conclusion, PTN was able to inactivate *C. tropicalis* biofilms under the action of blue-light, by means of Type I and II photodynamic mechanisms. Therefore, PTN can be a promising photosensitizer candidate for application in photodynamic therapy of *Candida* infections.

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Poster Po62

Fibroblastoid mammary carcinoma cells photoinactivation employing an anthraquinone from Argentinean flora

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Parietin (PTN), an anthraquinone (AQ) found in some vegetal species even lichens, has proven to be a good photosensitizer with promising applications in bacterial photoinactivation [1]. The aim of this work was to evaluate the *in vitro* activity of PTN as photosensitizer on a mammary carcinoma cell line in order to estimate its potential use in Photodynamic Therapy (PDT) of cancer.

PTN (1,8-dihydroxy-3-methoxy-6-methylanthraquinone) was isolated from the lichen *Teoloschistes nodulifer* (Nyl.) Hillman (Teloschistaceae) and it was purified by recrystallization from the acetone extract, and its purity was determined by HPLC.

We employed the murine mammary carcinoma cell line (LM2), originated from a mouse adenocarcinoma, and we determined: a) LD50: light dose inducing 50% of cell death after PDT treatment (at non cytotoxic concentration of PTN, irradiation time $\leq$ 30 min) by employing the MTT colorimetric assay; b) sub-cellular localization of PTN by fluorescence microscopy; c) cellular morphology after PDT by optical microscopy crystal violet staining; and d) impact of PDT on cell migration, using a wound healing assay. LM2 cells were used at semi confluency, PTN was prepared in RPMI medium with DMSO $\leq$ 1% and the irradiation doses were adjusted by employing different times of exposition to a light system, which consisted of 2 blue compact fluorescent lamps (Sica, 15 W).

Results show that PTN (purity of 91.2 ± 0.2%) has a cytoplasmic localization (1h incubation) and exhibited a LD50 of 0.95 J/cm2 (3 min). PTN-PDT induced morphological changes as well as condensed nuclei and cytoplasmic vacuolisation. Migration analysis suggested that whereas PTN *per se* induces a significant decrease on cell migration, migration index was impaired from 0.65 ± 0.04 to 0.30 ± 0.03 after PTN-PDT.

Therefore, this natural AQ that has a cytoplasmic target, induced cell killing mediated by photodynamic sensitization and impaired the *in vitro* migration rate of mammary carcinoma cells, at non cytotoxic concentrations and employing visible light.

The results of this work confirm the potential use of parietin in PDT, supporting the recommendations of the World Health Organization to revalue phytomedicine and consider the healing properties of the country's flora. Currently, we are carrying out *in vivo* studies of PTN-PDT on LM2 tumour bearing mice.

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Novel Magnetic Iron-Copper Nanocomposites as Photocatalysts for As(III) Oxidation

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At least four million people in South American countries drink water containing arsenic at levels that pose a risk to their health. Therefore, developing affordable and efficient techniques to remove As from drinking water is critical to protect human health.

We here employ magnetic iron and copper nanocomposites (NCs) as both adsorbents and photocatalysts for the oxidation of As(III) to the less toxic As(V) species. The synthesis of the NCs was made by following the precursor method[1],using bio-Based Substances (BBS), which are humic-like compounds, isolated from urban composting biowastes as complexing agents. The complexes of Fe^{3+} and Cu^{2+} with BBS were heated up to 400ºC in N_2.

Samples containing the NCs (A^{350} = 0.50) and 3 mM As (III) were irradiated for 60 min in a RPR Rayonet reactor containing 8 lamps with emission centered at 350 nm. The amount of As(V) determined by a colorimetric method[3] was larger in the air-saturated than in the Ar-saturated samples (Figure 1a). Laser flash-photolysis experiments (λ^{exc} = 355 nm) show the broad absorption characteristic of the formation of h^+/e^- upon irradiation. The reciprocal of the transient decay (τ) increases with increasing concentration of As(III) up to 0.5 mM and then reaches a plateau (Figure 1b), indicating a reversible one-electron oxidation of As(III) by h^+.

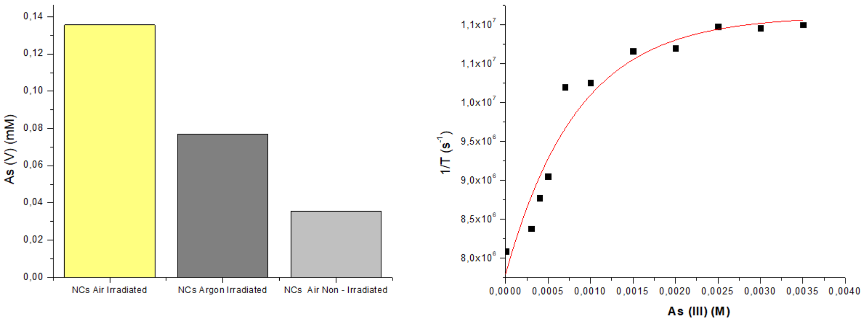

Figure 1: (a) As(III) concentration formed under different conditions. (b) Reciprocal of the electron/hole pair decay ($1/\tau$) vs. $[As(III)]_o$.

The amount of total As and As(III) were evaluated after irradiation of samples containing the NCs and As(III) to obtain information of the relative importance of the adsorption and photocatalysis routes for the removal of As with our NCs under different conditions.

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Poster Po64

Synthesis and characterization of Gold-silica-ICG nanostars with photothermal effect and reactive species generation.

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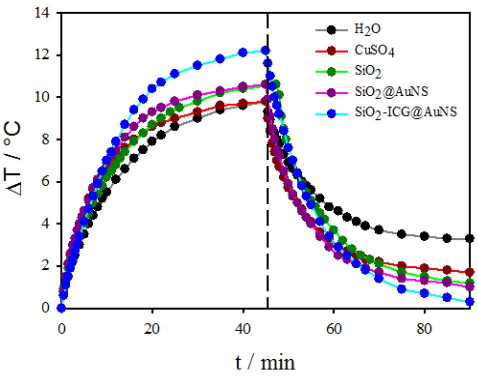
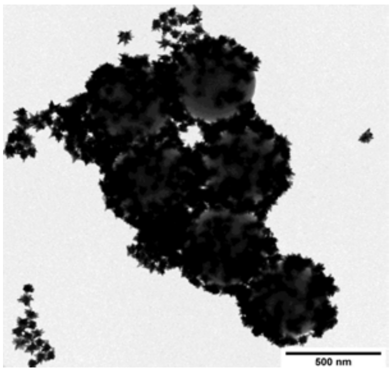
When light couples with the oscillation frequency of the conduction electrons in the metal nanopartcles (NP), a so called localized surface plasmon resonance (LSPR) arises, which is revealed by a strong absorption band along with an efficient photo-to-heat conversion [1].
Photothermal therapy (PTT) and photodynamic therapy (PDT) are promising cancer treatments in which photo-to-heat conversion by nanoparticles and the activation of a photosensitizer (PS) occur in response to applied laser light. As a result of the photoirradiation, cytotoxic photothermal heating and reactive oxygen species (ROS) can trigger apoptotic and necrotic cancer cell death [2].
Here we develop a multifunctional nanomaterial that could be used for simultaneously imaging and dual PTT and PDT treatment of the tumor.
We have synthesized and characterized SiO_2 NP funcionalized with gold NanoStars and Indocyanine Green (ICG), an amphiphilic carbocyanine dye that strongly absorbs and fluoresces in the NIR region of light, and produces singlet oxygen upon irradiation. The procedure employed for the synthesis of the nanomaterial was the layer-by-layer technique.
TEM images showed core-shell NP of 600 nm diameter. UV-visible absorption spectra showed that the LSPR of the nanoparticles is located between 600 and 900 nm. These wavelengths are within the NIR window, where light has its maximum depth of penetration in tissue. Suspensions of the unfunctionalized silica NP (SiO_2), silica NP decorated with gold nanostars (SiO_2@AuNS), and the NP containing both the gold nanostars and ICG (SiO_2-ICG@AuNS) were irradiated with a 800 nm laser and the temperature was measured at different irradiation times. Results showed that there is a photothermal effect for the suspensions of the gold-containing nanomaterials, since the temperature increase observed for these suspensions is larger than those observed upon irradiation of water and a calorimetric reference used for comparison. The production of singlet oxygen upon NIR irradiation was demostrated by employing the Singlet Oxygen Sensor Green probe. The generation of H_2O_2 was also investigated. These in vitro results seem to indicate that the nanomaterial is a good candidate to be employed in PTT and PDT.



Temperature profiles of different NPs, H_2O and $CuSO_4$



TEM images of SiO_2-ICG@AuNS

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New fluorescent probes as markers for biological mimicking media

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The 2,6-diphenyl-(4'-methoxybiphenyl)-N-alkylpyridinium perchlorates are organic compounds consisting of a donor group, a π-spacer and an acceptor group. These systems are characterized by showing an intramolecular charge transfer (ICT) from the donor unit to the acceptor unit, these probes exhibit high fluorescence, showing different emission wavelengths depending on the solvent.[1] This sensitiveness to the surrounding environment makes of them good candidates as markers of mimicking biological media. In order to test if these types of probes are compatible with biological systems, their photochemical and photphusical properties are evaluated in liposomes and in emulsions, understanding that these types of micro-structures emulate the chemical nature of the cell wall, a fact that allowed us to study the favorable interaction between the surface of the microheterogeneous system and the fluorescent probes.

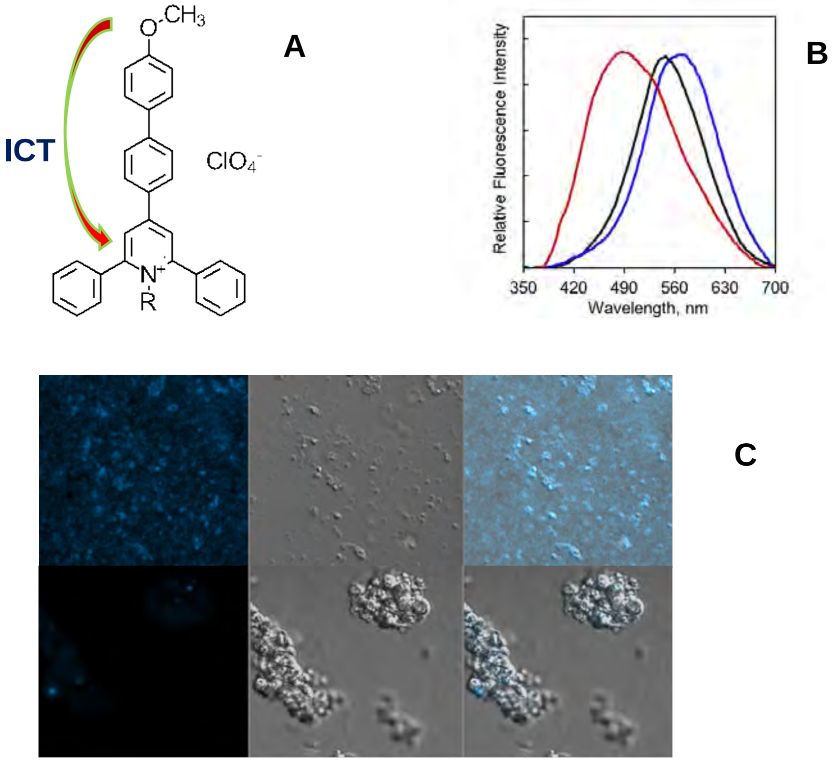

Figure 1: (a) structure of fluorescent probes (b) emission spectra in water (blue) octanol (black) and DMF (red). (c) micrographies of liposomes with fluorescent probe in blue.

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Poster Po66

Effect of chalcogen heavy atom substitution on the photophysical properties of tetrasubstituted zinc(II) phthalocyanines

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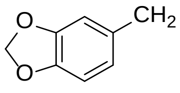
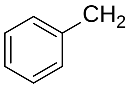
Photodynamic therapy (PDT) is a non-invasive and selective cancer treatment in which a photosensitizer generates singlet oxygen ($^1O_2$) as a cytotoxic agent under photoexcitation. Among suitable photosensitizers (Ps), zinc(II) phthalocyanines (Pc) are recommended for PDT due to their photostability, high absorption coefficient at long wavelengths, measurable fluorescence quantum yields (Φ_F), high triplet quantum yields (Φ_T), long triplet lifetimes (τ_T) and efficient singlet oxygen production (Φ_Δ) [1]. The amount of $^1O_2$ generated by Ps is regulated by the efficiency of a spin-forbidden electronic transition from the singlet to the triplet excited states. Besides, the presence of heavy atoms in a molecule is known to have an influence over the rates of this transition. Heavy atom effect has been exhaustively studied in Pc by the introduction of halogen atoms in order to increase Φ_Δ [2]. However, symmetrical tetrasubstituted halogenated Pc do not allow any further chemical modification in order to increase water solubility or reduce aggregation tendency. On the other hand, the introduction of different chalcogen atoms in Ps, such as the case reported for phenothiazinium dyes, has shown similar photophysical effects [3]. According to these evidences, we intend to explore the effect of chalcogen heavy atom substitution on the photophysical properties of tetrasubstituted Pc bearing different peripheral groups.

R	X	λ_{abs} (nm)	λ_{em} (nm)	Φ_F	τ_T (μs)	Φ_Δ
	O	683.5	686	0.08	177	0.67
	S	694.5	701	0.12	164	0.72
	Se	694.5	700	0.08	72	0.84
	O	683	686	0.23	144	0.66
	S	694	696	0.20	116	0.67
	Se	693	694	0.11	75	0.74
$HOCH_2CH_2$	O	683.5	690	0.16	164	0.58
	S	694	699	0.12	126	0.69
	Se	693	698	0.09	68	0.75

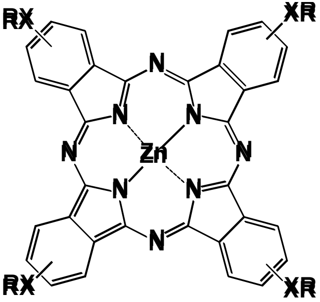


Table 1. Photophysical properties of Pc in DMSO

The presence of S and Se atoms produce a 9-11 nm bathochromic shift in UV-visible absorption spectra compared to O analogs. The introduction of heavier chalcogen atoms decreases Φ_F, increases Φ_Δ (by increasing Φ_T) and shortens τ_T. These effects, which are manifested in the order O < S < Se, can be explained in terms of spin-orbit coupling theory.

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Poster Po67

Photolysis of 17β-estradiol in alkaline seawater under UV-C radiation

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Between the recognized endocrine disruptors are natural and artificial estrogens like 17β-estradiol (E2), the most important secreted female sex hormone.

The entrance of these compounds in the aquatic environment through daily liquid wastes of society as well as pharmaceutical industries, and pathology laboratories leads to an increase in their concentrations in these resources.[1] E2 has one ionizable proton, therefore the study of its photodegradation in basic seawater is of interest.

Steady state photolysis of E2 in seawater in basic medium at 253.7 nm was studied following the decrease of the fluorescence intensity (excitation at 270 nm). Excitation-emission matrices (EEMs) with wavelengths from 240 to 350 nm and 250 to 400 nm for excitation and emission, respectively were analysed in combination with parallel factor analysis (PARAFAC).[2]

E2 was initially dissolved in absolute ethanol, and then diluted in seawater in the presence of 1 mM KOH. The final E2 concentrations ranged from $5x10^{-6}$ to $1x10^{-4}$ M.

Both ultraviolet absorption and fluorescence spectra were affected by the presence of alkali.

The irradiation of E2 in alkaline seawater produces spectral modifications, and a reduction of fluorescence intensity close to 60 % after 200 minutes was observed. These modifications were not observed in the dark.

These results suggest that the photodegradation in alkaline media is more effective. In seawater without the presence of KOH, a percentage of consumption of approximately 50 % in the same irradiation conditions was previously obtained.

Direct photolysis with UV-C radiation of E2 in seawater in the presence of KOH offers a promising alternative method to remove E2 from effluents prior to its discharge into the sea, reducing the irradiation time for more than half an hour.

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Study of the photodegradation of methylparaben and propylparaben in alkaline medium by 254 nm irradiation

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Photolytic degradation of the endocrine disruptors, methylparaben (MP) and propylparaben (PP), in alkaline medium upon 254 nm irradiation has been investigated. They are used as antimicrobial agents in pharmaceutical and cosmetic products. Given its environmental importance and presence in different aquatics environments, alternative methods for its elimination have been studied[1].
The reaction solution of MP initial concentration $2x10^{-4}$ M and PP $6x10^{-5}$ M was prepared in distilled water. The pH reaction medium was adjusted by a phosphate buffer for pH 11.
The photolysis was carried out for 120 minutes until conversion >10%, using radiation from a low pressure mercury lamp at 254 nm of 6 W of power at room temperature. The concentration changes of MP and PP, during photolysis were determined by UV-visible spectrophotometry and actinometry experiments were conducted using potassium ferrioxalate solution[2]. The absorption spectra of the aqueous solutions of MP and PP at pH 11 have a maximum for both at 296 nm. From the experiments carried out, the coefficients of pseudo-first order velocity and the quantum yield of photodecomposition (Φ) were determined in aerated solutions, with nitrogen bubbling, sodium azide and methanol as scavengers to quench oxygen singlet and hydroxyl radical, respectively. The results obtained in this work are summarized in the following table:

PBs	Solutions	$kx10^4$ (min^{-1})	Φ photodecomposition
MP	aerated	1.48±0.21	0.0031±0.0006
	nitrogen bubbling	1.15±0.59	0.0017±0.0008
	sodium azide	0.14±0.06	0.0019±0.0003
	methanol	0.48±0.12	0.0010±0.0007
PP	aerated	1.93±0.50	0.0012±0.0001
	nitrogen bubbling	0.48±0.080	0.0010±0.0001
	sodium azide	0.16±0.03	0.0003±0.0001
	methanol	1.35±0.42	0.0003±0.0001

The photodegradation of MP and PP in alkaline medium took place through direct photolysis under UV irradiation. Coefficients of pseudo-first order velocity values obtained show that degradation is inhibited for both with nitrogen bubbling, sodium azide and methanol, which suggest participation of reactive oxygen species.
The photodegradation of MP and PP in alkaline medium employing UV irradiation may emerge as viable alternative method for its elimination.

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Poster Po69

Fluorescence and Photodegradation of Petroleum Maltenes

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Maltenes are the normal alkane soluble fraction of petroleum and show a chemical composition similar to that found for the petroleum itself [1]. This fraction comprises resins, aromatic compounds, as well as straight, branched and alicyclic hydrocarbons.

The maltenes used in this study were extracted from a heavy crude oil from San Jorge Gulf basin (well B-483 from Cañadón Perdido field) with a density of 0.9307 ± 0.0001 g. mL^{-1} at 15 ºC (API degree 20.54) and a viscosity of 1941 ± 24 cp at 25°C. The maltenes content, obtained from crude oil based on the ASTM 2007 D method modified, was 95.71 ± 2.69 %. Solutions of maltenes in n-hexane were characterized using absorption and different modes of fluorescence spectroscopy (conventional, excitation, synchronous and total fluorescence spectra, EEM). In addition, the fluorescence quantum yield (Φ_F) in n-hexane, was obtained in air-satured samples and in solutions bubbled with nitrogen for 20 min, using quinine sulphate in 1.0 N sulphuric acid as standard (Φ_F= 0.546) [2].

Photodegradation of maltenes was evaluated using EEM in conjunction with parallel factor analysis (PARAFAC). Maltenes dissolved in n-hexane at a concentration of 2.78 mg. L^{-1}, were exposed to UV-A radiation for 2.5 hours. Solutions of maltenes in n-hexane between 0.78 and 3.64 mg. L^{-1} were used for the calibration and validation of the method. Control samples were kept in the dark during the same period. The EEM wavelength ranges were 280-500 nm for excitation and 300-570 nm for emission.

The profiles of the excitation and absorption spectra were similar, suggesting that the basic absorbing chromophores were the same. The maltenes emission spectra obtained consist of a structureless broad band in the visible region, from ca. 300 to 570 nm. The fluorescence quantum yield (λ_{exc}= 290 nm) of the maltenes fraction in air-satured samples was 0.13 ± 0.03, while for the solutions bubbled with nitrogen it was 0.38 ± 0.04.

The profiles of the EEM show that the emission maximum is centered near 379 nm (excitation around 280 nm). There was a 35.61 ± 2.40 % of reduction in the emission spectra area after 2.5 h of irradiation, while the non-irradiated blank remained relatively constant. In the same time period there was a slight decrease in absorption. By employing the EEM/PARAFAC method, the concentration prediction for the irradiated maltenes sample was 1.23 ± 0.03 mg. L^{-1}, using a model of 2 components. This change could be attributed to the compounds formed after opening of one or two aromatic rings [3].

The results presented here provide evidence that the petroleum maltenes from the San Jorge Gulf basin were significantly affected by the action of UV-A radiation.

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Photophysical Characterization of Phenalenone Derivatives

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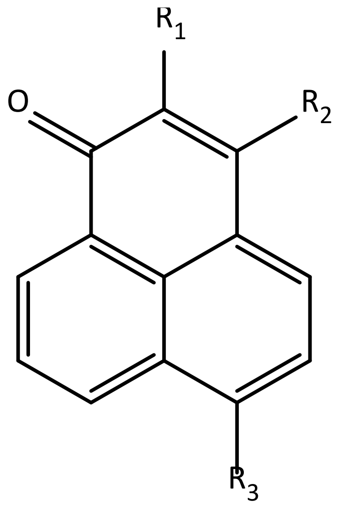
Phenalenone has been studied extensively due to its behavior and because it can be used on interesting applications from the scientific and technological point of view. We are interested in obtaining and characterizing phenalenone derivatives able to interact with specific targets, like lectins, to generate singlet oxygen promoting damage at specific selected locations, upon excitation preferably with visible light.
The presence of substituents on the molecule rearranges the molecular electronic states changing its photophysical behavior. To rationalize the effect of the presence of substituents in several positions of the phenalenone ring, we prepared and studied the derivatives shown in next table.



Molecule	R1	R2	R3
OXA2PN	Benzoxazole	-H	-H
3OHPN	-H	-OH	-H
3OEtPN	-H	-OEt	-H
6CGalPN	-H	-O(CH$_2$)$_6$Gal	-H
6CManPN	-H	-O(CH$_2$)$_6$Man	-H
6OHPN	-H	-H	-OH
6OEtPN	-H	-H	-OEt

When compared with phenalenone, the properties of the different compounds studied show the expected behavior, with bathochromic shifting of absorption and with the capability to generate singlet oxygen maintained or fairly reduced.

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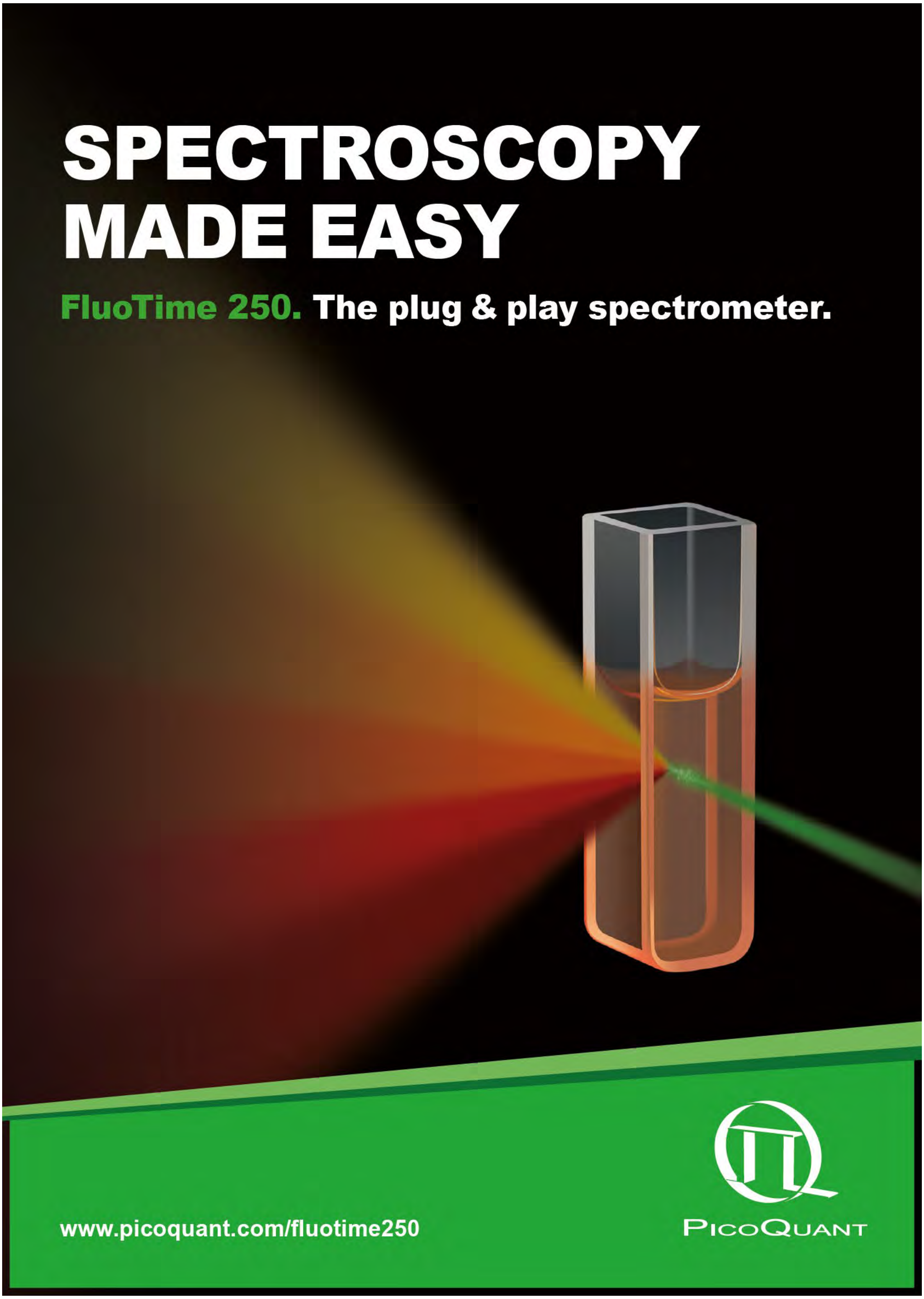

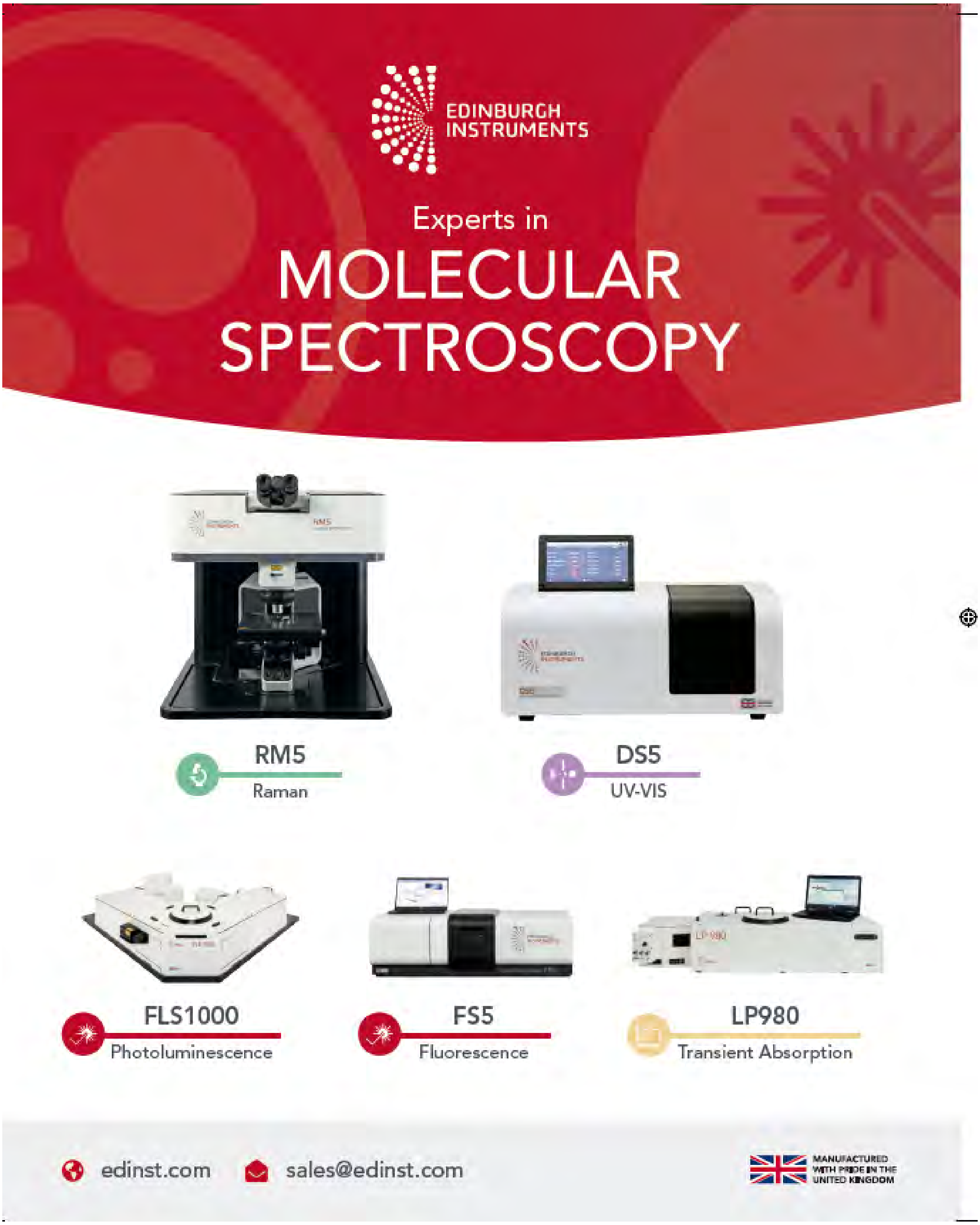
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