XIII Encuentro Latinoamericano de Fotoquímica y Fotobiología

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Book of Abstracts

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Symposium in honour of Dr. Norman A. Garcia (Andi)

This symposium in honour of Dr. Norman (Andi) Garcia originates as a recognition of his scientific trajectory and, above all, his human quality, by former co-workers and students of Andi.

Thanks to his commitment, he has not only trained many highly qualified human resources through the direction of Doctoral Theses and researchers, but also contributed to the creation of several research groups outside the National University of Río Cuarto. In this way, he achieved the introduction of photochemistry in national universities in which this discipline had not previously been addressed, such as the National Universidad Nacional de la Patagonia Austral at Río Gallegos, the Universidad Nacional de la Patagonia San Juan Bosco at Comodoro Rivadavia and in the Universidad Nacional de San Luis. This contribution materialized not only in the training of human resources but also in the assembly of laboratory facilities through the donation of equipment.

Dr. Garcia directs and has directed numerous projects related to basic and applied photochemistry, which has led him to establish an active exchange of researchers from both home and abroad research.

Andi has made his teaching career at the Chemistry Department at the Universidad Nacional de Río Cuarto, becoming Emeritus Professor in 2016.

Is one of the first Doctors that graduated in the UNRC and his work of doctoral thesis was directed by the Dr. Carlos Mario Previtali. In 1985 he entered as a research assistant CIC-CONICET being promoted to Senior Researcher (Investigador Superior) in June 2013.

He has completed the direction of twelve PhD theses in chemistry, in addition to three co-directions, four postdoctoral fellowships and four CIC-CONICET members.

He has established successful international research collaborations, mainly with groups from Germany (1982-1990) and Spain (1990-2011).

His disciples occupy prominent positions as professors of National Universities and as members of the Career of the Scientific Investigator of CONICET.

His dedication, high capacity of work, pragmatism and his subtle sense of humour, to name just a few of his qualities, make Dr. Norman García an invaluable person

Speakers:

Dra. Silvia Braslavsky

Director of the Postdoctorate of Dr. García in the Max Planck Institut fuer Strahelenchemie

"Cómo re-encontramos el oxígeno molecular singlete con Andi en Muelheim"

Dr. Gustavo Argüello - Full Professor (UNRC)

Dr. García's colleague, together began the study of singlet oxygen at the National University of Cordoba

Un, dos, tres..... así de fácil

Dr. Daniel Mártire – Full Professor (UNLP)

Dr. Garcia's colleague. They collaborated on numerous research projects.

Efecto de nanopartículas de Ag, Au y Ag/Au sobre la fotofísica de Riboflavina

Dra. Susana Criado - Adjunct Professor (UNCR)

First PhD in chemistry directed by Dr. García at the UNRC

Degradación de fármacos y aditivos alimentarios mediado por ROS

Dra. Adriana Pajares – Full Professor - (UARG-UNPA and UNPSJB)

PhD in chemistry directed by Dr. García. Under the direction of Andi, they created the area of photochemistry in the UARG-UNPA

Fotodegradación de contaminantes del agua mediada por oxígeno singlete

Dra. M. Isela Gutiérrez. - Associate Professor (UNPSJB)

PhD in chemistry directed by Dr. García. Under the direction of Andi, they created the area of photochemistry in the UNPSJB

Fotoquímica de productos de interés en la región patagónica

Dra. Paulina Montaña – Adjunct Professor (UNSL)

PhD in chemistry directed by Dr. García. Under the direction of Andi, they created the photochemical area in the UNSL

Desde San Luis, unas palabras de gratitud

Symposium in honour of our mentor and friend Eduardo Lissi

Speakers: *Emilio I. Alarcón, Carolina Aliaga, Alexis Aspee, María Victoria Encinas, Julio de la Fuente, Miguel Neumann, Carlos Previtali, Tito Scaiano.*
Discussion leader: *Silvia Braslavsky*

Memories and anecdotes of the scientific experiences and discussions as well as of the friendship with our early guide and ever present mentor will be presented by the speakers in this symposium.

Since our starting in 1963 in Buenos Aires up to this day (2017) many scientific ideas were born out of the very basic, deep, sometimes “passionated discussions” with, and led by, Eduardo Lissi. He always had a brilliant hint and a “fundamental consideration” that often opened the way to novel areas of research. We learned that complex problems were frequently resolved with very simple, yet brilliant, ideas.

Eduardo was the organizer of the first ELAFOT in 1982 and was always very active in all the ELAFOT meetings. It is then very appropriate that we take the opportunity in our 13th-ELAFOT to congratulate him on his 80th birthday.

Although scattered in many parts of the world, Eduardo’s disciples have always taken great pleasure in discussing with him scientific problems. His scientific leadership and personal friendship has influenced our lives for over five decades well beyond the niche of science.

We wish Eduardo many more years of good life with Dorita and his marvelous family and we look forward to having many more inspiring discussions with Eduardo.

Acknowledgments: The support received from FONDECYT (Chile) is acknowledged by C.A. (Grant N° 1160486), A.A. (Grant N° 1140240) and J. de la F. (Grant N° 1150567). M.V.E. acknowledges Grant Anillo ACT 1412 (CONICYT).

PLENARY LECTURES

PL1- Derivados Fenólicos en la Vida Cotidiana y las Consecuencias de su Footooxidación

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El fenol (F) y derivados (DF) están presentes en un sinnúmero de productos que de manera directa o indirecta impactan en nuestra vida cotidiana. F es obtenido a gran escala a partir del derivado de petróleo cumeno, e industrialmente se lo emplea como intermediario en la fabricación de otros materiales de amplia difusión. Basta señalar la profusión de DF en la industria química con especial mención en la agroquímica, farmacéutica, textil, de plásticos, de pinturas y de explosivos. En este contexto no es difícil imaginar la frecuencia y volumen de incorporación no deseada de DF en nuestro ecosistema, como resultado de la eliminación indiscriminada de deshechos domiciliarios e industriales, y las derivaciones que estos procesos conllevan. [1]

Es ampliamente conocido el efecto nocivo de F y DF sobre mamíferos y otras especies en casos de toxicidad aguda, cambios histopatológicos, mutagenicidad y carcinogénesis. Paralela y paradójicamente diversos DF constituyen biomoléculas esenciales en seres vivos, tales como vitaminas, proteínas, hormonas y neurotransmisores para mencionar algunas. [2]

Incorporados al ecosistema como contaminantes o bien formando parte de organismos vivos, los DF están sujetos a cambios, especialmente promovidos por reacciones químicas-térmicas, fotoquímicas y procesos microbiológicos. Los mismos, ya sean naturales o programados constituyen un punto de interés que ha sido abordado por la ciencia desde hace ya varias décadas. En particular, nuestro Grupo ha trabajado en el tema de las transformaciones fotoquímicas naturales-medioambientales y artificiales-programadas de un gran número de contaminantes y biomoléculas conteniendo DF. [3],[4] En esta charla trataremos de transmitir los puntos salientes y algunas contribuciones de nuestra labor en este campo, a lo largo de varios años. Se tratará de un enfoque hacia la importancia de la información obtenida por estudios cinéticos y mecanísticos de eventos fotooxidativos y el aprovechamiento y consecuencias de dichos procesos.

Agradecimientos: Esta presentación es el resultado del esfuerzo de muchas personas durante mucho tiempo, cuyos nombres sería imposible incluir en este espacio. Agradezco profundamente a todos ellos por su dedicación y honestidad.

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PL2- Photochemistry of Drug-Biomolecule Complexes

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This presentation deals with the photochemical behavior of the non-covalent complexes formed upon interaction between photoactive drugs and transport proteins or DNA. Transport proteins, such as serum albumins (SAs) or α-1-acid glycoproteins (AAGs) are carriers of endogenous and exogenous agents in the bloodstream and play a crucial role in relevant processes of living organisms. Hence, binding of drugs to transport proteins is an important issue, which can be addressed by different methodologies. Thus, we have employed the triplet excited states of a variety of drugs, generated by laser flash photolysis (LFP), as reporters for the microenvironments experienced within the protein binding sites [1-2]. This concept has been applied to determine the degree of drug binding and to investigate the distribution of a drug among several intraprotein compartments and the bulk solution. Moreover, the protein binding sites contain well-defined domains with specific amino acid residues capable of acting as catalytic sites, thus they can be used as appropriate nanoreactors to perform selective photochemical processes [3-4]. As regards DNA, it can interact with the UVA or visible fractions of sunlight through photosensitization by exogenous chromophores. These chromophores, which are present in a number of drugs, may extend the "active" region of the solar spectrum, increasing the probability of developing skin cancer. In this context, we have focused our attention on the drug-photosensitized formation of cyclobutane pyrimidine dimers (CPD), a type of DNA lesion that is difficult to repair [5-6]. One of our main findings is that the value of the thymine triplet energy is significantly lower in the DNA biomacromolecule than in the free base or in the isolated nucleoside [5]. The crucial role of drug/DNA complexation in the formation of CPD has been demonstrated using femtosecond and nanosecond transient absorption and emission measurements, in combination with in vitro DNA damage assays [7].

Financial suppport by the Spanish Government, the Regional Valencia Government, and the European Union is gratefully acknowledged.

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PL3- Type I and II Photosensitized Oxidation Reactions: Basic Reactions and a Novel Lipophilic Alkyl-Chain Pterin

Maurício da Silva Baptista,[a] Sarah J. Belh,[b,c] Sergio M. Bonesi,[d] Jean Cadet,[e] Paolo Di Mascio,[a] Ashwini A. Ghogare,[b,c] Alexander Greer,[b,c] Michael R. Hamblin,[f-h] Carolina Lorente,[i] Silvia Cristina Nunez,[j] Martha Simões Ribeiro,[k] Andrés H. Thomas,[i] Mariana Vignoni,[i] Niluksha Walalawela[b,c] and Tania Mateus Yoshimura[k]

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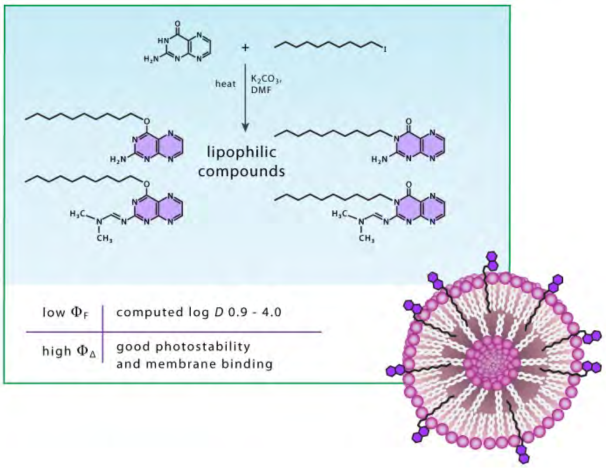

This lecture will present ten guidelines for a standardized definition of type I and II photosensitized oxidation reactions [1]. Because of varied notions of reactions mediated by photosensitizers, a checklist of recommendations will be provided for their definitions. Type I and type II photoreactions are oxygen-dependent and involve unstable species such as the initial formation of radical cation or neutral radicals from the substrates and/or singlet oxygen ($^1O_2$ $^1\Delta_g$) by energy transfer to molecular oxygen. Examples will be provided to illustrate the complexity and the diversity of the degradation pathways of mostly relevant biomolecules upon one-electron oxidation and singlet oxygen reactions [2]. Examples will also be chosen from our recent work on a new series of decyl chain [$-(CH_2)_9CH_3$] pterin conjugates [3]. These conjugates were synthesized in a regioselective coupling of the alkyl chain to the *O* site over the N^3 site. The *O*-alkylated pterin has been used to convert to the N^3-alkylated pterin under basic conditions, pointing to a kinetic product in the former and a thermodynamic product in the latter. Studies of adducts show an *N*-amine condensation of DMF solvent molecule as by products and help explain the origins of photobleaching stability. The new pterins have potential use in biomembranes and serve as a starting point where the synthesis can be expanded to produce novel lipophilic, photooxidatively active pterins.

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PL4- Photodynamic Action: New perspectives on the microbial control and cancer treatment

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Photodynamic action is a general principle involving the excitation of a photossensitezer by light and the energy transfer to molecular Oxygen, promoting a spin change and produzing a singlet molecule with high potential to oxidation. Photodynamic Action for biological effects is a growing field of research and, today, is present in many areas of health science. In this presentation we shall demonstrate the use of such reaction in the microbiological control either for infections or enviroment decontaminatiton as well as for the Cancer treatment. A few multicenter studies will be analysed showing the great potential of the technique and its advantages. The necessity of special instrumentaion for correct illumination of tissue is one of the limitation os such applications. We shall discuss a collection of experiments on the prove of principles part as well as for clinical applications. References for this work can be found at the page http://cepof.ifsc.usp.br

PL5- Photo-induced damage to cellular DNA: formation and mechanistic insights

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Direct excitation of nucleobases by UVB radiation and to a lesser extent by UVA photons is implicated in the formation of the three main classes of bipyrimidine photoproducts including cyclobutane pyrimidine dimers (CPDs), pyrimidine (6-4) pyrimidone lesions and their Dewar valence isomers. Evidence is provided that UVB irradiation of isolated DNA in aqueous solutions and in cells gives rise to the predominant generation of cis-syn cyclobutane pyrimidine dimers (CPDs) together with pyrimidine (6-4) pyrimidone photoproducts (6-4PPs), whose formation is strongly primary sequence dependent [1]. A notable change in the photoproduct distribution is observed when DNA either in the dry or in desiccated microorganisms is exposed to UVC or UVB photons with an overwhelming formation of 5-(α-thymidyl)-5,6-dihydrothymidine, also called "spore photoproduct" (dSP) at the expense of CPDs and 6-4PPs. UVA irradiation of isolated and cellular DNA gives rise predominantly to bipyrimidine photoproducts through direct excitation of the bases with the overwhelming formation of thymine containing cyclobutane pyrimidine dimers at the exclusion of 6-4PPs. UVA photons have been shown to modulate the distribution of UVB dimeric pyrimidine photoproducts by triggering the isomerization of the 6-4PPs into related Dewar valence. Efforts have been made to assess the contribution of oxidative pathways to the overall DNA damage induced by UVA and UVB components of solar radiation [2]. This may include UVA-mediated sensitized reactions and delayed biochemical responses such as inflammation and bystander effect. In that respect UVA radiation appears to be much more efficient than UVB in inducing immediate oxidatively generated damage to the bases and 2-deoxyribose moieties of cellular DNA. The UVA-induced formation of 8-oxo-7,8-dihydroguanine is rationalized mostly in terms of selective guanine oxidation by singlet oxygen generated by type II photosensitization mechanism through excitation of still unknown cellular chromophores. In addition, hydroxyl radical ($^{\bullet}OH$) whose formation may be explained by Fenton type reactions subsequent to initial generation of superoxide anion radical ($O_2^{\bullet-}$) and its dismutation into hydrogen peroxide (H_2O_2), contributes in a minor way to UVA-mediated DNA degradation. This leads to the formation of both oxidized purine and pyrimidine bases together with DNA single strand breaks (SSBs) at the exclusion however of direct double strand breaks. No evidence has been provided so far for the implication of delayed oxidative degradation pathways of cellular DNA. As a plausible scenario, initial formation of $O_2^{\bullet-}$ and nitric oxide may generate peroxynitrite ($ONOO^-$) as the precursor of carbonate anion, an efficient one-electron oxidant of guanine. Thus putative characteristic UVA-induced DNA damage could include single base lesions, SSBs and more complex lesions arising from the initial formation of guanine radical cation. Support for the significant participation of oxygen and nitrogen reactive species has been provided by the delayed formation of CPDs in the DNA of melanocytes upon exposure to UVA radiation. It was recently proposed by Brash et al [3] that the mechanism of this dark photochemical reaction involves generation of $ONOO^-$ that would trigger melanin oxidation followed by formation of dioxetane, chemiexcitation and subsequent triplet energy transfer to the nucleobases.

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PL6- Photophysics of Dyes in Heterogeneous Systems

Enrique San Román

Instituto de Química Física de los Materiales, Medio Ambiente y Energía (INQUIMAE/CONICET-UBA) and Departamento de Química Inorgánica, Analítica y Química Física (FCEyN-UBA), Buenos Aires, Argentina
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Recent results on the photophysics of dyes adsorbed or included into inert and semiconducting microparticles and layer-by-layer self-assembled and spin-coated polymer thin films will be summarized. Emphasis will be given to the effect of the supporting environment and dye-to-dye interactions at dye loadings up to 1 M and to the trade-off between light absorption and energy dissipation by real or virtual traps on increasing dye concentration.

Some of this work was performed on systems characterized by the presence of light scattering. Solids composed by microcrystalline cellulose microparticles – an air-tight, light-scattering environment – were the workbench on which methods to quantify absolute fluorescence and triplet quantum yields, fluorescence reabsorption and reemission, and energy transfer and trapping were developed and tested [1]. Whenever needed, these methods will be briefly described.

Following cases will be addressed:

1. Fluorescence studies on several dyes included into cellulose showed that the maximum distance among dye molecules at which energy trapping takes place – the quenching radius – is 12-15 Å. Space heterogeneity arising from the coexistence of amorphous and crystalline domains was explored by time resolved fluorescence and phosphorescence spectra of xanthene dyes. Tokyo Green increases strongly its fluorescence quantum yield in cellulose due to inhibition of photoinduced intramolecular electron transfer. In some cases, while fluorescence quantum yields are a decreasing function of dye concentration because of energy trapping, triplet quantum yields remain nearly constant. Dye-to-dye charge transfer assisted triplet formation has been postulated in such cases.
2. Studies on the photocatalytic reduction of Cr(VI) on TiO_2 modified by an Al phthalocyanine is very efficient, in spite of the aggregation of the dye on the semiconductor surface, and independent of dye loading. Photocurrent and fluorescence action spectra demonstrated that the monomeric photoactive dye and inactive dye clusters are coupled by a micelle-like equilibrium on the TiO_2 surface, rendering the chemical potential of the monomer almost independent on dye loading.
3. The high degree of organization resulting from layer-by-layer self-assembly of positively charged poly[diallyldimethylammonium] chloride and negatively charged Rose Bengal molecules reduces the formation of dye aggregates to 55 % at effective dye concentrations near 1 M. Though aggregation and energy trapping, self-assembled thin films are able to yield fluorescence and singlet molecular oxygen. On the other hand, Fluorescein incorporates to a lesser extent and does not show dye aggregation. Dye hydrophobicity increases film stability, aggregation tendency and energy trapping.
4. Thin films ($\sim$200 nm) composed of xanthene dyes embedded into poly(2-hydroxyethyl methacrylate) were studied in a very broad dye concentration range: 0.0002 to 0.4 M. For Phloxine B, fluorescence and singlet oxygen quantum yields, which are constant at low concentrations, are proportional to each other and fall off around 0.01 M. Rose Bengal builds up imperfect (fluorescent) energy traps and significant quantum yields are obtained up to 0.1 M. Quenching radii obtained by modeling are again around 15 Å. The efficiency in the production of excited states, defined as fluorescence quantum yield × absorption factor has therefore a maximum at intermediate concentrations, 0.025 M for the first case and 0.15 M in the second one. The amount of singlet oxygen reaching the film surface is independent of film thickness, as the diffusion length within the polymers is in the order of some tens of nm.

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INVITED LECTURES

IL1- Organoboron fluorescent dyes: are there alternatives for Bodipy?

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The design of novel fluorescent dyes with optimal photophysical performance and high (photo)chemical stability is a steadily growing demand on organic chemists. Tetracoordinate organoboron dyes have been in the focus of these efforts and are nowadays particularly represented by boron dipyrromethene dyes (BODIPY) [1,2]. The extraordinary high molar absorption coefficients and emission quantum yields have made these dyes a preferred choice for applications in bioimaging and in materials chemistry. However, one of the disadvantages of BODIPY dyes is their small Stokes shift, which may be a problem in fluorescence microscopy. Although this may be avoided by employing energy-transfer antennae [1,3], the need for alternative boron-containing architectures is evident.

Tetracoordinate *N,N*-, *N,O*- or *N,C*-chelate organoboron fluorophores with significant Stokes shifts, often based on intramolecular charge transfer, could be a worthy alternative to BODIPY dyes [4,5]. In our own research program we have focused on organoboron dyes with arylisoquinoline as tunable π-system, resulting in BAI dyes (borylated arylisoquinolines) [6-8]. BAI dyes have large Stokes shifts, solvent-dependent emission spectra, moderate to high fluorescence quantum yields, and sometimes appreciable two-photon absorption cross sections in the near-infrared region.

Other efforts were directed towards boronic-acid derived chelate dyes with salicylidenehydrazone ligands (BASHY dyes), which are easy to prepare and functionalize for a multitude of potential applications [9-11]. Among their most interesting photophysical properties are their high brightness (molar absorption coefficient × emission quantum yield) and significant two-photon absorption above 800 nm. The contribution will showcase some applications (molecular thermometry, molecular logic, bioimaging) and contextualize the dyes' photophysical and photochemical performance.

The financial support by the Spanish MINECO, Madrid (grant CTQ2014-54729-C2-1-P), the European Regional Development Fund (ERDF), and the Junta de Andalucía (grant P12-FQM-2140) is gratefully acknowledged. The work was done in collaboration with the authors mentioned in the references 3, 6-11.

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IL2-Photochemical Approaches to Build-up Heterocyclic Compounds

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Among the principal elements that comprise all drugs (carbon, hydrogen, oxygen, or nitrogen), sulfur represents the fifth most prevalent element in overall architectural representation and biological significance. Sulfur compounds are used in clinical diseases, such as depression, arthritis, diabetes or cancer [1]. Many sulfur-containing compounds with biological activity are heterocycles, and their syntheses represent an important challenge to the Organic Chemists.

In this context, synthetic organic photochemistry constitutes a research area with exceptional importance to the development of efficient and selective transformations to prepare natural products as well as molecules with high structural complexity [2]. A central feature of all light-promoted transformations is the involvement of electronically excited states, formed upon the absorption of photons. This excitation leads to a significant of the reactivity of a chemical compound, offering a smart way to generate reactive intermediates under controlled conditions.

In this work, exploring photoreactivity of different sulfur compounds to obtain new heterocycles derivates with relevance to biological systems will be presented. Specifically, polycyclic sultams and benzosultams, were obtained in good yields by photocycloaddition reactions (Figure 1).

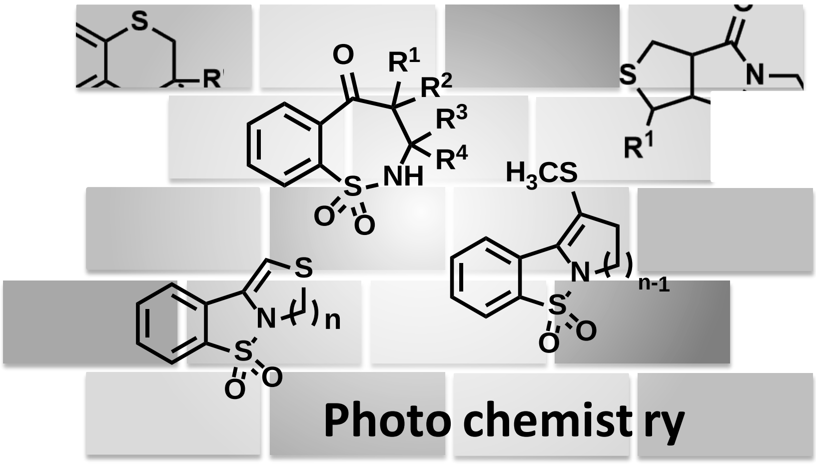

Figure 1

Finally, recent approaches to the synthesis of thiocromane and tetrahydrothiophene scaffolds using photochemical means, as well as continuous flow systems will be discussed.

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IL3- Photochemical deposition of silver nanoparticles on clay and bionanocomposites films.

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Silver nanoparticles (AgNPs) have been studied in recent years because of their strong surface plasmon absorption in the visible region. Furthermore, AgNPs have become a target of great interest due to their remarkable electronic, optical, mechanical, magnetic, chemical and antimicrobial properties. These properties, depends on the size and type of AgNPs, which influences their application[1,2].

Photochemical method was used to synthesize AgNPs in the presence of citrate or different clays (Laponite B, SWy-1 and Barasym) as stabilizers and Lucirin TPO as photoinitiator. This methodology was a good tool to obtain AgNPs quickly. The uniform and small size AgNPs can be prepared by fast (up to 60 min) photochemical synthesis by using clays. The structure in stacked parallel layers of SWy-1 along with a small size of AgNP favors antimicrobial activity of the material [3].

AgNPs were synthetized on films of chitosans/montmorillonite nanocomposites also by photochemical method. Nanocomposites were prepared using chitosans with different molar masses and deacetylation degrees, as well as modified with hydrophobic and hydrophilic. TEM images revealed AgNPs with spherical morphology for all films. The increase of clay concentration resulted in faster synthesis of AgNPs and nonuniform nanoparticles size with aggregation of some particles. The film of modified chitosan presented smaller and more uniform nanoparticles size along mixture of exfoliated and intercalated structures. All nanocomposite-AgNPs films inhibited the growth of *Escherichia coli*and *Bacillus subtilis*[4].

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FAPESP (2012/19656-0), CNPq(490421/2013-0, 401434/2014-1)

IL4- Electron-catalyzed Radical Perfluoroalkylation of Organic Sulfides: The Serendipitous Use of the TMEDA/I2 Complex as a Radical Initiator

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Perfluoroalkyl sulfides have found wide applications, such as in liquid crystal displays, for oleophobic surface coatings, as well as in the synthesis and development of potential hypotensive agents for clinical use containing SR_F moieties such as Losartan derivatives (Dup 753).

Particularly, the case of pefluoroalkylated thiosugar derivatives, where the sulfur atoms in thioaldoses make the interglycosidic bonding stable to glycosidases. The incorporation of a hydrophobic chain as aglycone, such as a perfluorinated residue, could have a high impact in protein–carbohydrate recognition events which take place between sugars and glycosidases, glycosyltransferases and also lectins. For these reasons, fluorinated thiosugars have a great potential as tools in the field of Glycobiology. To that effect, we proceeded to studying the S-perfluoroalkylation of thiocarbohydrates. The reactions of the sugar thioaldoses 2,3,4-tri-*O*-acetyl-1-thio-β-D-glucuronic acid methyl ester and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranose under our standard reaction conditions, afford 75 and 83 % yields of SC_4F_9 -substituted products, respectively. The disaccharide 2´,3´,4´,6´,2,3,6-hepta-*O*-acetyl-1-thio-β-D-cellobiose affords product in 50 %. However, the reaction of galactoside-disulfide (1,1´-bis-(2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranose)) did not afford any $S\text{-}C_4F_9$ substitution product.

In this work, we will show the serendipitous discovery of a radical initiation event from visible light irradiation of a complex between TMEDA and I_2 (i.e. :[(TMEDA) $I.I_3$]) which triggers an electron-catalyzed process towards the synthesis of perfluoroalkyl sulfides of biological potential in improved substitution yields. We will also discuss the applications to such perfluorinated thiosugar derivatives.

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IL5- Intrinsic Photosensitizers for DNA Damage Formation and Repair

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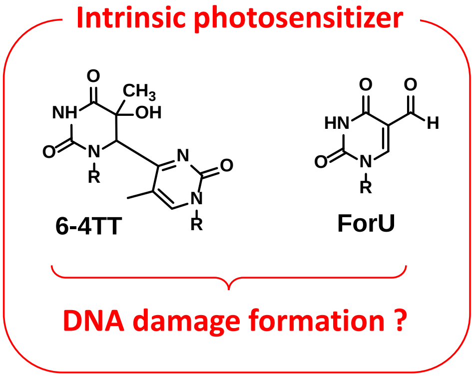
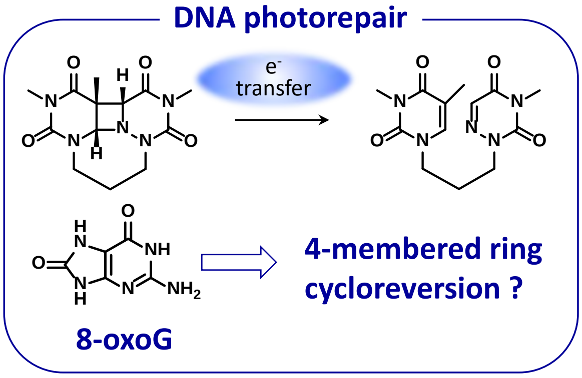
The DNA of all living organisms is continously damaged by endogenous processes as well as by exogenous genotoxic chemicals and physical agents. Solar UV radiation has been recognized as the most important and ubiquitous carcinogenic physical agent in our natural environment. In this context, the knowledge of the DNA photodamage and photorepair is a central topic as it has been established that exposure to solar ultraviolet radiation is involved in the pathologies of carcinoma and melanoma.

Recently, we have centered our attention on the potential of some DNA lesions to behave as intrinsic photosensitizers capable of generating chemical changes in their neighborood, and inducing this way multiply damaged sites known as clustered lesions. Here, our recent outcomes obtained through the combination of analytical, photophysical and biochemical techniques will be reported in connection with the study of two thymine-derived lesions absorbing in the UVA, namely the (6-4) photoproduct (6-4TT) and the 5-formyluracil (ForU).[1-2]





Moreover, we will also address one of the processes involved in DNA repair by intriguing enzymes called photolyases, which take advantage of sunlight to restore lesions like cyclobutane pyrimidine dimers or (6-4) photoproducts. In particular, the photoreductive process responsible for the splitting of the azetidine ring, proposed as an intermediate during (6-4) photoproduct repair at thymine-cytosine sequence, will be considered through the study of a model formed by photocycloaddition between thymine and 6-azauracil.[3-4] In this context, the redox properties of the main DNA oxidative lesion, namely 8-oxoguanine, will be exploited to split the 4-membered ring compounds, acting this way as a "beneficial" intrinsic photosensitizer.

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IL6- Betalains: from fluorescent flowers to functional dyes

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Sunlight provide plants with the energy necessary to produce oxygen from water and carbon dioxide. There are, however, several other intriguing phenomena involving the interaction of light and plant pigments. When irradiated with blue light, the yellow petals of most plants of the order Caryophyllales emit green fluorescence[1]. Although the ecological and biological functions of fluorescence in plants is still matter of debate[2], this result contributed to promoting interest in water-soluble chromoalkaloids called betalains[3].

Betalamic acid is the key biosynthetic precursor of red betacyanins and yellow betaxanthins, the two classes of natural betalains. The aldimine coupling between betalamic acid and cyclo-DOPA produce betacyanins, which have been used as antioxidants and show gene regulatory activity[4]. Betaxanthins are formed when cyclo-DOPA is replaced by other amino acids or amines and show high biodisponibility. Betalains are imines or iminium salts and, therefore, are subject to hydrolysis and transimination[5]. Consequently, betalamic acid have been obtained from the hydrolysis of natural betalains (especially betanin, the main pigment of beetroots) and used to semisynthesize natural and artificial betalains.

Our research group have developed synthetic routes to a variety of functional semisynthetic derivatives and analogs of betalains[6–9]. In my talk, I will present our results on the design and semisynthesis of betalains, neobetalains and quasibetalains and their application as smart fluorescent probes and as mediators in energy conversion systems.

Acknowledgments

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IL7- Mechanistic Diversity for the Dynamics of Cucurbit[n]uril-Guest Complexes

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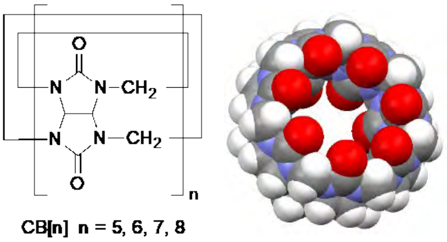
Cucurbit[n]urils (CB[n]) form high affinity complexes with positively charged and hydrophobic guests. We observed and defined that the mechanistic diversity for CB[*n*] complex formation is a consequence of guest size and the presence of cations that bind to the carbonyl-lined portals of CB[*n*]s. The 2-naphthyl-1-ethylammonium cation (NpH+) binds to free CB[7], and Na+ cations slow the binding dynamics by complexing CB[7].[1] Guests can slip into the CB[7] cavity, as is the case for NpH+, or larger guests form exclusion complexes where the guest's positive charge interacts with the portal without immediate inclusion of the hydrophobic moiety of the guest into the CB[7] cavity.[2] Different roles were observed for the Na+ cations. The cation can cap both portals of the CB[n] removing the ability of the host to bind the guest and slowing the reaction, while in other cases Na+ can interact with the guest@CB[n] complex expelling the guest and therefore enhancing the rate of the relaxation kinetics.



Higher complexity was observed with the *N*-phenyl-2-naphthylammonium cation as a ditopic guest, where the naphthyl moiety fits optimally into CB[7] and the phenyl group is expected to bind more weakly. Following these expectations, at low Na+ concentrations, the CB[7] complex with phenyl inclusion was observed only transiently. In contrast to NpH+, the PNA naphthyl moiety binds with CB[7] and CB[7]•Na+, making the PNA residence time inside CB[7] sensitive to the Na+ concentration. Unexpectedly, at high Na+ concentrations, the inclusion of the phenyl group was stabilized by Na+ capping, causing the dynamics of phenyl and naphthyl binding to be competitive. This switch in mechanism with Na+ concentration provides an example of systems chemistry, where a change in the concentration of a "bystander", Na+, changes the outcome of the reaction, i.e., the type of host-guest complex formed.

Kinetic studies are also instrumental in developing CB[n] systems as functional supramolecular systems and three proof of principle examples will be presented: (i) development of an assay to determine the association and dissociation kinetics for spectroscopically silent guests using competitive kinetics, (ii) determination of the guest ground-state protonation/deprotonation rate constants for the guest@CB[7] complex as an elementary reaction in catalysis[2] and (iii) use of CB[6] as an additive in hydrogels to alter the distribution of small molecules between the gel's network and the constrained aqueous phase.

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IL8- From marine molecules to the ideal sunscreen: what do the photophysicochemical studies tell?

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It is well recognized that skin cancer can be prevented by reducing intentional exposure to UV radiation and improving photoprotection strategies. Topical application of sunscreens is the most widespread protective practice. Sunblock lotions typically contain a mixture of different types of organic and inorganic UV filters to ensure effective protection throughout the UVA and UVB spectra. However most commercial options have limited efficiency, they are not stable, or produce harmful reactive intermediates during energy dissipation pathways and thus pose risks to the environment and human health [1]. Hence, a novel kind of shields against sun rays based on natural sunscreens is emerging, that could protect not only people, but also textiles and outdoor materials [2]. Marine metabolites such as mycosporine-like amino acids (MAAs) have attracted great interest in relation to their photoprotective potential. High photostability in aqueous solution and efficient dissipation of the absorbed radiation energy as heat have been verified for MAAs isolated from algae. On the other hand, structurally and biosynthetically related to MAAs, there is gadusol, a metabolite that can be extracted from fishery debris. In addition to the intense absorbance in the UVB and the high photostability in water, gadusol efficiently deactivates radicals and electronically excited species (photosensitizers, singlet oxygen) and exhibits redox properties similar to those of ascorbic acid [3].

Appropriate solubilization and vehiculization of the active molecules is expected to be required in any innovative development based on these natural resources. This usually may convolve microheterogeneous systems where still the problematic of the safety of complex ingredient mixtures remains and the risks of phototoxic responses should be evaluated [2,4]. Thus, detailed descriptions of the physicochemical, photophysical and photochemical properties of MAAs and gadusol in more complex environments than aqueous solution are needed.

We have carried out a series of photophysical and photochemical experimental studies in the last years with the goal of exploring the influence of different micellar and polymeric environments, as well as structural modifications on the MAAs shinorine and porphyra-334 and gadusol. This report will focus the effects on the protective ability against UV of the marine molecules and the factors that may contribute to improve the performance of novel sunscreen systems.

Acknowledgments: Financial supports from Universidad Nacional de Mar del Plata (EXA 759/16-15/E710) and CONICET (PIP 2014-0804) are greatly acknowledged.

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IL9- Industry-Academia Collaborations in the Development of Photoredox Reactions That Generate C-S, C-N, and C-C Bonds

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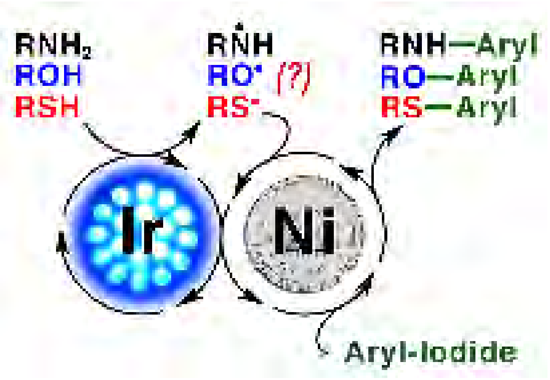
The recent surge in reported photoredox transformations is strongly driven by industrial interest, and made possible by the availability of bright blue LED light sources. Several pharmaceutical companies, including Pfizer and AstraZeneca, are developping and employing novel photoredox reactions that continue to appear in the literature at increasing rates.

This talk will present parallel industrial and academic approaches that gave rise to new carbon-sulfur, carbon-nitrogen and carbon-carbon bond-forming photoredox reactions. In particular, mechanistic investigations of iridium and nickel co-catalyzed cross-coupling reactions that yield C-S and C-N bonds will be presented in detail.[1,2] The excited-state and redox chemistry of Ir(III) catalysts has been investigated; this traditionally academic approach helped develop carbon-carbon cross-coupling reactions with a similar strategy. To reduce the cost associated with iridium-based catalysts, organic dyes with absorption in the visible, strong excited-state oxidation potentials, long-lived excited-state lifetimes and good photostability are introduced as alternatives with some success.

As an example of a traditional industrial approach, high-throughput screening of photoredox reactions led to the discovery of an inexpensive manganese catalysts that, in some cases, can yield quantitative carbon-carbon bond-forming reactions. In this reaction, a Mn(0) dimer, $Mn_2(CO)_{10}$, is photochemically cleaved to generate mild $Mn(CO)_5$ radicals. These radicals can quickly abstract iodide from alkyl iodides ($MnCO_5$ + iodocyclohexane, $k_{abs} = 7.6 \times 10^5$ $M^{-1}s^{-1}$, $\Delta G^{\ddagger} \sim 17$ kcal/mol). Several outcomes are possible once the carbon-centered radicals are formed, and synthetically useful applications will be presented.



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IL10- Colloidal Lead bromide Perovskites as promising luminescent nanomaterials

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Lead halide perovskites materials with a general formula $APbX_3$ (A= organic or inorganic cation and X= halide anion, Figure 1a) are of great interest due to their unique optical properties (broad absorption band, high optical absorption coeficient and narrow emission spectrum), excitonic properties and electrical conductivity making them very useful for photovoltaic applications and luminescent device preparation.[1] Colloidal nanocrystals of $CH_3NH_3PbBr_3$ have been prepared for the first time by using long ammonium salts as organic ligands and they exhibited good luminescence quantum yield (20 %).[2] A fine-tuning of the molar ratio between the precursors and organic ligands gave rise to an enhancement of their luminescence up to 83% (Figure 1b).[3] More recently, we have demonstrated that the use of a quasi-spherical shaped 2-adamantly ammonium bromide (AD), as the only organic ligand, produces the highest luminescent quantum yield (~100 %) of colloidal perovskites nanocrystals ($CH_3NH_3PbBr_3$@AD), a narrow emission peak ca. 520 nm (Figure 1c) and long luminescence lifetime with the longest component in the microsecond scale. [4]

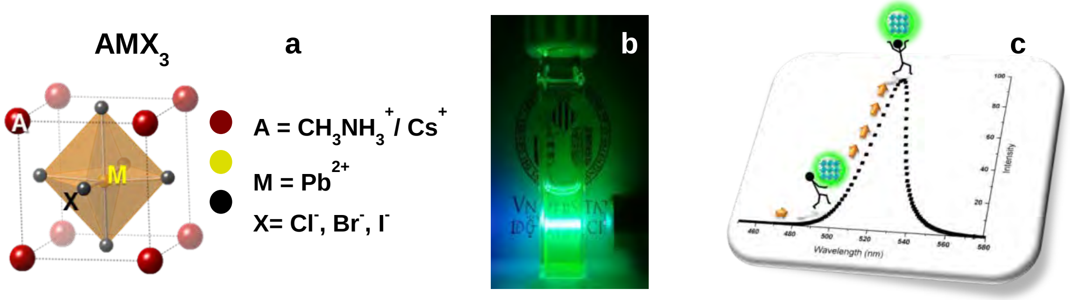

Figure 1: General structure of perovskite material (a), picture of colloidal $CH_3NH_3PbBr_3$ nanocrystals under visible light excitation (b) and emission spectrum of colloidal $CH_3NH_3PbBr_3$@AD nanocrystals in toluene (c).

Interesting, formation of host-guest complexes on the nanoparticle surface by using cucurbit[7]uril (CB[7]) produces photostable nanoparticles (PK@AD-CB), which not only preserve the perovskite photoluminescence but also exhibit enhanced stability under contact with water. These structures can be very promising materials for the preparation of luminescence devices.[5]
The alkyl organic ligand plays an important role in the formation, stabilization and photophysical properties of colloidal $CH_3NH_3PbBr_3$ perovskite nanocrystals. A general overview of the colloidal perovskites applications will be discussed.

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IL11- Photochemistry of Rhenium Complexes Bearing P,N-Bidentate Ligands

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It is now very well established that following excitation with UV-Vis light, Re^{I}-diimine complexes, $[(N,N)Re(CO)_3X]$, mainly yield a triplet metal-to-ligand charge transfer excited state (^{3}MLCT). This is due to the extremely fast intersystem crossing process from the singlet to the triplet excited state, taking place normally in a few hundred femtoseconds and having a quantum yield of the unity.31-33 Then, the ^{3}MLCT-excited state decays to the ground state by radiative and/or non-radiative processes or experiences a photochemical reaction to give products. Additionally, when molecular oxygen is present in the media, energy transfer from ^{3}MLCT to oxygen may occur, then generating the reactive singlet excited state of the molecule, $O^{2}(^{1}\Delta_g)$. Regarding these routes, it is surprising that despite of the great amount of research related to ReI-diimine complexes, the photoproduct or reactive species generation, remain largely unexplored, moreover overruling their 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 this 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**) (Scheme 1).[1-3] In this work, we present the kinetic and the photochemistry of these mononuclear complexes followed by UV-Vis or IR spectroscopy, exploring the posibility of singlet oxygen or carbon monoxide generation.

Acknowledgements: Authors acknowledge financial support from Fondecyt 1160749, PIA Conicyt Anillo ACT 1404, and UNAB DI-1253-16/R.

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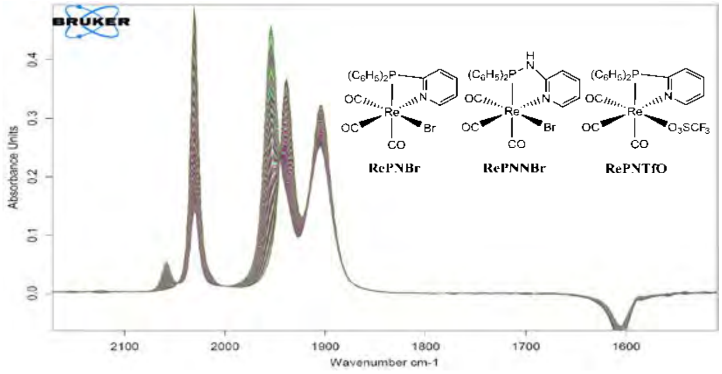

Scheme 1. Photolysis of RePNBr followed by IR and structure of the studied complexes.

IL12- Design and synthesis of fluorescent molecular probes and their applications

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Fluorescent probes are widely used in the biologically-related disciplines and continues to grow, because it allows investigation of samples in situ and provides information with high spatial and temporal resolution. Fluorescent dyes are of particular importance because of their small size, possibility to finely tune their properties, and ease of chemical modification and functionalization. Fluorescent molecular probes are dyes that are specially designed to perform biosensing or bioimaging. Some probes can specifically target biomolecules whereas others enable detection and imaging of analytes.

In my group, we are interested on the development of dyes that changes their emission characteristics in response to environmental properties such us polarity and viscosity or under irradiation with light. Solvatochromic 3-hydroxychromone (3HC) derivatives exhibit dual-color emission and thus a ratiometric response due to Excited-State Intramolecular Proton Transfer (ESIPT). They constitute very versatile and sensitive probes of environmental properties such as polarity and hydrogen-bonding capacity. BODIPY (boron difluoride dipyrromethene) is immensely popular and has many uses and application due to bright fluorescence, tunable emission spectra from visible to near-infrared, robustness and vast possibilities of funtionalization. In particular, meso-BODIPY detivatives leads to variation in emission by rotation of the meso phenyl ring with respect to dipyrromethene core allowing to map viscosity enviroment. Diarylethene derivatives possess very efficient, reproducible and fatigue resistant photochromicity – a bimodal, reversible, photo-induced transition between two states with different absorption properties. When paired with a fluorescent donor, diarylethenes can act as switchable Förster resonance energy transfer (FRET) acceptors. Various constructs including organic dyes or quantum dots as donors have been reported in the literature. We have denoted this phenomenon as photochromic FRET (pcFRET). Sulfone derivatives of diarylethenes display fluorescence in one (closed form) of two thermally stable photochromic states.

A very important objective of our work is the design and synthesis of fluorescent molecular probes as a ligand- fluorescent probe to target specific proteins, as sensor of changes in environment and combined with other imaging and therapeutic modalities for theranostic applications.

SHORT LECTURES

SL1-Hybrid supramolecular photosensitizers in functional microscopy and PDT

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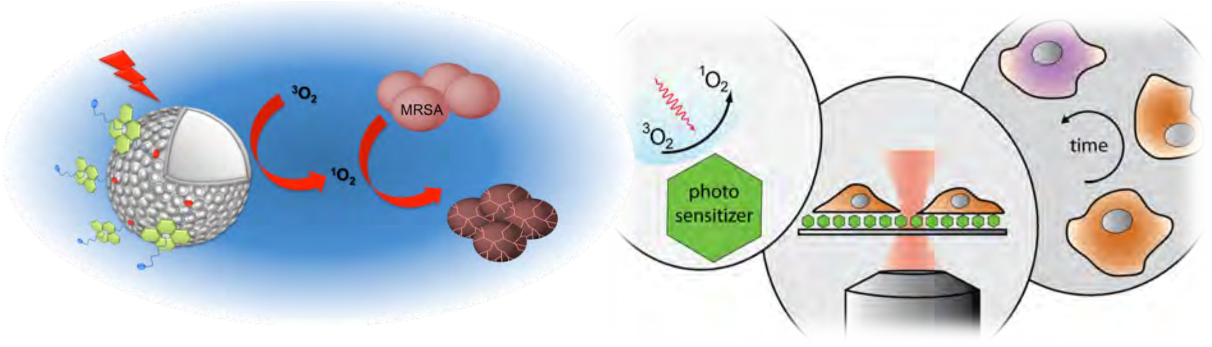

Figure 1 – Left side: Supramolecular arrays against MRSA. Right side: Photosensitizing substrates for functional microscopy.

A careful molecular design has allowed us to fully control the aggregation of planar photosensitizers and to tune their photophysical properties for applications in phototherapy and functional microscopy (**Figure 1**).

We have recently designed a series of hybrid nanomaterials able to target, to label and to photoinactivate pathogenic and antibiotic resistant bacteria. The surfaces were functionalized with a Si(IV) phthalocyanine derivative that forms reactive oxygen species upon irradiation with red light. In this sense, it was possible to avoid the stacking of the phthalocyaninates by axially binding them to the surface of aluminosilicates [1,2] and layered nanoclays [3,4]. Currently, we are extending these concepts to targeted, fully soluble and biodegradable platforms, a prerequisite for biomedical applications. These approaches include the use of dextrin conjugates [5] and cyclodextrin vesicles [6] that selectively photoinactivate Gram-positive strains. We have also implemented light-driven arrays for spatiotemporally resolved functional microscopy to monitor in situ the response towards ROS of eukaryotic [7] and prokaryotic [8] cells.

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SL2- Supramolecular Control of Singlet Oxygen Generation Using Cucurbit[*n*]urils

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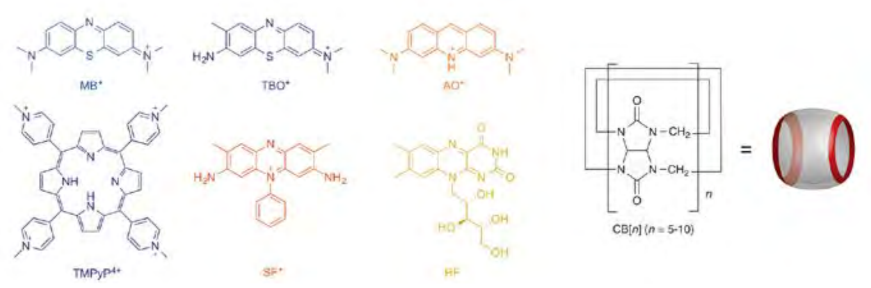
Singlet oxygen, O_2 $^1\Delta_g$ or commonly $^1O_2$, is a reactive oxygen species (ROS) involved in many applications in biology and medicine. One of the most important areas of research involving $^1O_2$ is photodynamic therapy (PDT), which combines photoactive drugs (photosensitizers) with light and oxygen to induce cellular death of abnormal tissue due to the generation of $^1O_2$ and other ROS.[1]
For the last few years our group has been investigating the effect of the encapsulation of photosensitizers into molecular containers of the family of cucurbit[*n*]urils, (CB[*n*], *n* = 5-8 and 10), which have great potential as drug delivery vehicles for PDT and other biomedical applications.[2-5]



Scheme 1. Some photosensitizers reported in the literature to bind to CB[*n*]s.

Complexation of photosensitizers with CB[*n*]s show several characteristics that are ideal for PDT, such as enhanced singlet oxygen generation, resistance to photodegradation, stability against enzymatic degradation and no aggregation. Currently we are studying in detail the influence of CB[*n*]s on the photochemistry of photosensitizers by laser flash photolysis using transient absorption and $^1O_2$ luminescence. Key points into the effect of the CB[*n*]s and the characteristics of the photosensitizer will be discussed. Knowing this properties, we have developed a $^1O_2$ supramolecular switch that allows us to turn *on* and *off* $^1O_2$ generation.

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SL3- Searching for new strategies against *Candida tropicalis* biofilm: natural photosensitizing anthraquinones in combination with Amphotericin B

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Candida tropicalis is increasingly becoming one of the most commonly isolated pathogens in fungal infections, with a significant decrease in its susceptibility to antimicrobial agents, apparently due to its capacity for biofilms formation [1, 2]. Among the different postulated strategies for the treatment of biofilms, combination of drugs has achieved to improve results [3]. Another estrategy in development is the antimicrobial photodynamic therapy (aPDT), especially to combat infectious agents that have developed resistance to classical treatments. This theraphy inactivates microorganisms by means a biological photo-oxidation mediated by reactive oxygen species (ROS) [4]. Previously, we have demonstrated the *in vitro* photodynamic effect of two natural photosensitising anthraquinones (AQ), rubiadin (**AQ1**) and rubiadin 1-methyl ether (**AQ2**), over *C. tropicalis* biofilms. **AQ1** produced a 63.5% of reduction (%R) in the biofilm biomass of *C. tropicalis* NCPF 3111 at 1.96 µg/ml, and **AQ2** achieved a 47 %R of the the biomass at 15.6 µg/ml. It was also established that this effect was related to an increase in the oxidative and nitrosative stress[5].In this work, we have studied different strategies to improve the antibiofim activity of AQs. In this sense, the effect of consecutive irradiation periods on biofilms trated with each photosensitintizing AQ was assessed. In addition, the combination of each AQ with Amphotericin B (AMB), and the combination of both AQ with each other, even under different irradiation conditions, was evaluated. Generation of reactive oxygen species (ROS) and reactive nitrogen intermediate (RNI) was also measured, studying the activation of superoxide dismutase enzyme (SOD) and the total antioxidant system response.

It was possible to reduce the bioactive concentration of both AQs, by applying consecutive irradiation periods (15 min light) during incubation (0, 3, 6, 24, 27 and 30 h). In addition, this irradiation procedure allowed enhancing the antibiofilm effect of **AQ2** (62.9 %R), since this AQ reached a higher accumulation percentage in the biofilm compared to **AQ1** at 3 h of incubation (22.4 % *vs.* 1.22 %). Furthermore, when each AQ was used in combination with AMB under irradiation, the antifungal activity upon *C. tropicalis* biofilms was potentiated, by reducing the bioactive concentrations. The two AQs and AMB were used at concentrations below the photoactive Minimal Inhibitory Concentration (pMIC), specifically at their pMIC/2 defined as pSubMIC. Consecuently, this reduction in the photoactive concentrations would allow decreasing the side effects of AMB. Similar potentiation was observed when the AQs were combined with each other upon photo-stimulation. Even the antibiofilm effect of the combinations was further potentiated when the frequency of irradiation was increased, specifically for rubiadin 1-methyl ether that achieved 82 %R in the biomass of the biofilms. All observed effects were related with a redox imbalance in biofilm.

Therefore, the combination of an antifungal agent with photosensitizing compounds that allow the application of aPDT, would be a new strategy to improve the activity of antifungal drugs like AMB, becoming an alternative for the development of more effective and safe antifungal treatments.

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SL4- Chromophores á la carte, simple methods for the preparation of complex fluorescent materials

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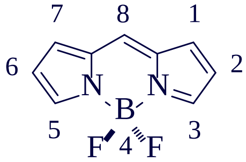
Truly remarkable applications of dipyrromethene-BF_2 fluorophores **1** (BODIPYs®) [1] continue to appear in the literature. These fluorescent compounds were first reported by Treibs and Kreuzer in 1968.[2] Little did they know about the great impact these analogues were to have in so many disciplines. The properties of this family of compounds are reported in excellent reviews.[3]



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Some relevant examples of their applications include the tagging of biomolecules, as components of supramolecular light-harvesting systems, in the construction of dye sensitized solar cells, as sensors, as components of fluorescent nanocars, as nanoparticle conjugates, as ligands for human β-adrenoceptors, as components of bulk heterojunction solar cells, in real-time PCR methods, and to visualize Langerhans islets, and as a quality control in milk, among others.

Thus, there is a need for the development of new synthetic methodology to prepare BODIPY derivatives with tailored properties such as λ_{abs}, λ_{fl}, Stokes shifts, solubility, etc. Ideally, this methodology should also allow for the attachment of functional groups that could be used to anchor the BODIPy core to target molecules.

In this presentation, three new methods to achieve the above-mentioned objectives will be presented:

a) The use of orthogonal reactivity to build complex BODIPY analogues [4]
b) Arylation reaction of polyhalogenated Biellmann BODIPYs
c) The use of multicomponent reaction to build complex BODIPY derivatives [5]

Acknowledgments: We wish to thank CONACyT (Mexico), and the University of Guanajuato for financial support, and Cuantico de Mexico (www.cuantico.mx) for kind donation of starting BODIPY derivatives.

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SL5-Some Models for Luminescence in Lanthanide-doped Solids

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We will show some of our models to account for the luminescence emitted by solids doped with cations of lanthanide metals [1-7]. Beginning with a brief review of some fundamentals regarding to luminescent materials, their technological uses and photophysical processes involved in them, we will focus on Lanthanide (Ln) -doped crystals and glasses, and on Ln-doped semiconductors, such as ceramic materials. In Ln-doped crystals and glasses occur phenomena of energy transfer, which give rise to processes such as frequency up-conversion, energy migration, cross relaxation, etc. They can be investigated with respect to the quantum-mechanic interactions that produce them, as well as with respect to the series of individual and collective dynamic events affecting to the optical centers involved. For this we dispose of some statistical-mechanic models that describe and predict the observed luminescence. On the side of Ln-doped ceramic materials, among others, thermoluminescence processes could be present. We will show the case of the thermoluminescence glow curves analysis of pure and CeO_2-doped Li_2O–Al_2O_3–SiO_2 glass ceramics.

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SL6- Photosensitized oxidation of 2'-deoxyguanosine 5'-monophosphate: mechanism of the competitive reactions and product characterization

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UV-A radiation (320–400 nm) induces modifications to different biomolecules through photosensitized reactions[1]. Oxidized pterins are efficient photosensitizers that accumulate in the skin affected by vitiligo, and photoinduce the oxidation of guanine in a process initiated by an electron transfer from the nucleobase to the triplet excited state of the photosensitizer[2]. In this work, we have investigated the degradation of 2'-deoxyguanosine 5'-monophosphate (dGMP) photosensitized by pterin (Ptr), the parent compound of oxidized pterins, in aqueous solutions under UV-A irradiation. We identified five products containing the oxidized guanine moiety: the deoxyribonucleoside 5'-monophosphate derivatives of imidazolone (dIzMP), dehydroguanidinohydantoin (dDGhMP), guanidinohydantoin (dGhMP), oxazolone (dZMP) and spiroiminodihydantoin (dSpMP). Additionally a product denoted P680 according to its molecular weight was detected. P680 consists of one molecule of dGMP linked to one molecule of dDGhMP. This product presents an absorption band in UV-A region, and it can fluoresce with a maximum at 440 nm (Figure 1).

The experimental results show that the degradation mechanism of dGMP is initiated by an electron transfer from dGMP to the triplet excited state of Ptr ($^3\mathrm{Ptr}^*$) yielding the corresponding pair of radicals: $\mathrm{Ptr}^{\bullet-}$ and $\mathrm{dGMP}^{\bullet+}$. Reaction of the latter, in its deprotonated form, with superoxide anion leads to dIzMP, which then yields dZMP. 8-Oxo-7,8-dihydroguanosine 5'-monophophate (8-oxo-dGMP) is also formed from $\mathrm{dGMP}^{\bullet+}$ and then rapidly oxidizes to dDGhMP and dGhMP. The higher molecular weight product P680 is also formed from $\mathrm{dGMP}^{\bullet+}/\mathrm{dGMP(-H)}^{\bullet}$ and its rate of formation increases when $O_2^{\bullet-}$ is eliminated. This fact indicates that in type I photooxidation of dGMP, new products not well characterized up to now, are formed upon elimination of $O_2^{\bullet-}$. This situation is very common in biological systems due to the presence of quenchers of this reactive oxygen specie. Finally, dSpMP, the only product arising from the oxidation of dGMP by $^1O_2$, is a minor product of the dGMP photosensitized degradation under our experimental conditions.

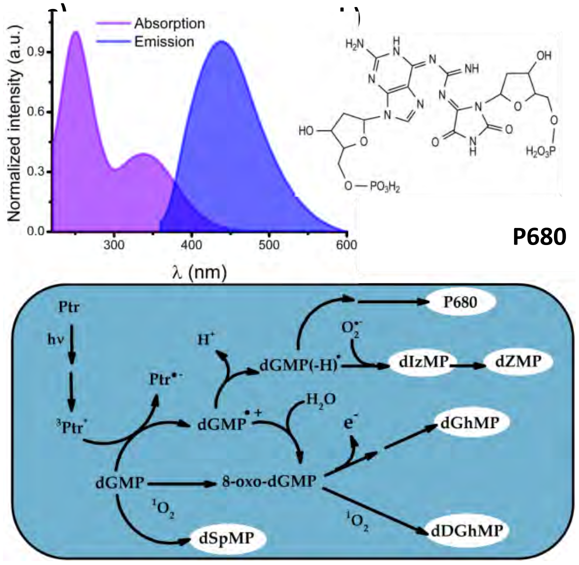

Figure 1. a)*Spectroscopic features of P680. Absorption and emission spectrum of P680 (λexc = 330 nm).* ***b)*** *Proposed chemical structure of product P680.* ***c)*** *Scheme of dGMP photosensitized oxidation via type I (electron transfer) and type II (oxidation by* $^1O_2$*) mechanisms.*

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SL7- Photocatalytic performance of pallladium-modified TiO_2: from UV to visible light organic transformations

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Visible-light-mediated photo-redox catalysis has emerged as a valuable concept in organic synthesis to induce selective organic transformations avoiding the undesired photo degradation of organic molecules under UV light exposure. Titanium dioxide (TiO_2) is a well-known semiconductor and its use as a photocatalyst has been widely explored as an alternative heterogeneous photoredox catalyst. Heterogeneous photo-catalysis is a promising technology providing both facile catalyst separations, and potential reuse. The main disadvantage of the use of pure nanometric TiO_2 as a photocatalyst is the large band gap (>3.1eV) of this semiconductor that can only absorb UV light (<400 nm). Decorating TiO_2 with noble transition metals such as Pd, Au or Cu, among others, can overcome this problem as the resulting materials usually absorb light in the visible region.

We present here our efforts to develop hybrid catalysts based on TiO_2 decorated with noble metal or metal oxide nanoparticles, with emplasis on palladium, which can be suitable catalysts for different organic transformation under mild conditions. The first example involves Pd/PdO NPs-doped TiO2 catalyst, known as an efficient photo-catalyst for olefin hydrogenation in the absence of H_2 gas upon UV irradiation. Its photocatalytic activity can be tuned in favour of hydrogenation or isomerization of benzyl-substituted alkenes simply by changing the irradiation wavelength. The isomerization can be thermally induced in air or driven by visible light irradiation at room temperature under Argon atmosphere, while switching to UV irradiation leads to efficient hydrogenation. The versatility of the catalyst is also tested for Sonogashira and Ullmann couplings upon visible light irradiation.

SL8- Molecular imaging and PDT-mediated therapy of bacterial infections with maltodextrin-based probes: A question of structure and stability

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Early diagnosis and localization as well as treatment of bacterial infections is a big challenge in daily clinical routine as multiresistant pathogens become increasingly relevant. Addressing a bacteria-specific metabolic pathway, such as the maltodextrin transport mechanism, would be the most promising way to detect small or even hidden colonies *via* non-invasive imaging techniques (PET or SPECT). It also provides the possibility for treatment using targeted photodynamic probes.

We developed a maltohexaose-conjugated Si(IV) phthalocyanine (***AGA156***) against bacterial lesions. Unexpectedly and most interestingly, we found with the aid of time-resolved confocal microscopy that the photoprobe adheres to the bacterial cell wall. Despite clearly targeting the maltodextrin transporter, it is not actively carried into Gram- (*E. coli*) and Gram+ (*S. aureus*) strains.[1] Luminescence lifetime measurements with a maltodextrin-conjugated phosphorescent Pt(II) complex (***AGA287***) underlined these findings. Whilst this binding characteristic still facilitates visualization, it results in a superficial bacterial labelling, as opposed to the amplification strategy *via* accumulation proposed by the literature.[2]

Further *in vivo* experiments with a maltohexaose-decorated SPECT-tracer, [^{99m}Tc]***MB1143***, yielded a defined accumulation at the area of infection with *S. aureus*. This was complementarily accompanied with a clearly defined uptake of [^{18}F]FDG mediated by inflammatory cells, showing the associated response of the surrounding tissue. Therefore, we can nicely distinguish between infection and inflammation. However, for the detection of even small affected areas, it is necessary to have a metabolic accumulation of the tracer and therefore an amplifying signal.

Our probes also showed that the anomeric centre of the carbohydrate must remain unaffected to elicit a metabolic trapping. Therefore, we also developed a fast synthetic route for different ^{18}F-labelled maltodextrins (maltotriose up to maltohexaose) with a non-blocked anomeric centre. We evaluated their stability regarding starch-degrading enzymes in the blood plasma. We found that maltotriose is the best scaffold for the development of maltodextrin-based probes addressing the bacteria-specific transporter. Thus, different ^{18}F-labelled maltotrioses were synthesized and are currently under evaluation. The unblocked anomeric centre, serum stability and the possibility for true metabolic uptake and accumulation shoud result in an amplified signal with an enhanced sensitivity.

This work was supported by grants from the Deutsche Forschungsgemeinschaft (DFG), CRC656 (MoBil, project A10) and Cells in Motion, Cluster of Excellence (CiM, FF-2013-10; CiM-IMPRS)

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SL9- Integration of Temperature and Blue-Light Sensing in *Acinetobacter baumannii* Through the BlsA Sensor

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BlsA is a BLUF photoreceptor present in *Acinetobacter baumannii*, responsible for modulation of motility, biofilm formation and virulence by light. In this work, we have combined physiological and biophysical evidences to begin to understand the basis of the differential photoregulation observed as a function of temperature. We show that *blsA* expression is reduced at 37°C, which correlates with negligible photoreceptor levels in the cells, likely accounting for absence of photoregulation at this temperature.

Another point of control occurs on the functionality of the BlsA photocycle itself at different temperatures, which occurs with an average quantum yield of photoactivation of the signaling state of 0.20±0.03 at $15°C < T < 25°C$, but is practically inoperative at $T > 30°C$, as a result of conformational changes produced in the nanocavity of FAD. This effect would be important when the photoreceptor is already present in the cell to avoid almost instantaneously further signaling process when it is no longer necessary, for example under circumstances of temperature changes possibly faced by the bacteria.

This complex interplay between light and temperature would provide the bacteria clues of environmental location and dictate/modulate light photosensing in *A. baumannii*.

This work has been supported in part by grants from Agencia Nacional de Promoción Científica y Tecnológica de Argentina (PICT 2012-2666, PICTO-UNSE 2012-0013, PICT 2013-0018 and CT 2014-1161).

SL10- Silicon Based Biomimetic Dyads: Photophysics and Charge Separation Processes

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Charge separation is one of the important steps in the photosynthetic process involved in the transformation of solar energy into chemical potential. Such strategy has inspired different approaches which nowadays are defined as artificial photosynthesis [1]. These involve the design and assembly of devices for the direct production of solar fuels, photo-electrochemical application in fuel cells, and the engineering of enzymes and photoautotrophic organisms. Also, lately nanotechnology contributed to the field with new active materials for energy conversion, re-engineering some devices to make them more efficient [2]. In line with this idea, in the present work we report the design, synthesis and photophysics of novel dyads using silicon nanoparticles (Si nps) and typical organic chromophores, in order to obtain charge separated states.

Si nps of different sizes were synthesized by thermal oxidation of metallic silicides [3] and functionalized with allylamine using hydrosilylation reactions. After that, amine-terminated Si nps were reacted with carboxyl derivatives of tetra-mesitylporphyrins, carotenoids or diketopyrrolopyrroles. The assemblies were characterized using HR-TEM, XPS and FTIR, and studied using UV-VIS absorption and emission spectroscopic techniques, either time resolved and steady state.

Experimental results were analyzed relying on Marcus theory of electron transfer reactions.The electron transfer rate constants depend on the size of Si nps and they are strongly affected by the linking strategy employed, clearly reflecting the effects of quantum confinement and electronic coupling. These results constitute the photochemical basis for applications of these dyads in high surface area photoelectrodes for solar energy conversion.

Acknowledgments

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SL11- Shedding New Light into Lipid Oxidation in GUVs and Bacteria. From Membrane Dynamics to Cell Survival.

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Lipid oxidation is a ubiquitous process with important roles in cell biology and consequently in human health. Lipid oxidation may involve a chain autooxidation reaction, may take place via enzymatic pathways or via photooxidation. Chemical modifications to the lipid molecule may be amplified as changes in collective physical properties such as lipid membrane surface area, thickness, porosity, permeability, and segregation. In this presentation, we will describe the use of fluorescence microscopy jointly with a fluorogenic α-tocopherol analogue probe previously developed by us (H_2B-PMHC) to study oxidation of lipid membranes in giant unilamellar vesicles (GUVs) mediated by photoinduced generation of singlet oxygen ($^1O_2$). Fluorescence microscopy studies with $^1O_2$ photosensitizers on single GUVs embedding H_2B-PMHC illustrated rapid activation of the probe followed later by fluctuations of the lipid membrane and expansion. A correlation was observed between the time for antioxidant H_2B-PMHC consumption by $^1O_2$ (directly related to the rate of lipid oxidation) and the onset of membrane fluctuations. We also expand our studies from GUVs to bacteria where our microscopy tools enable us to illuminate the spatiotemporal ROS production due to oxidative stress induced by ciprofloxacin in individual bacteria. Discussion on the biological relevance of these processes will be presented.

SL12-Concerted One-Electron Two-Proton Transfer Processes (E2PT) in Models Inspired by the Tyr-His Couple of Photosystem II

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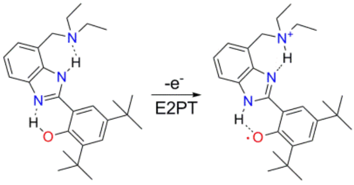

Figure 1

In photosystem II the amino acid pair Tyr$_Z$-His acts as a redox mediator between P680 and the oxygen evolving complex where water oxidation takes place. Upon oxidation Tyr$_Z$ donates a proton to its hydrogen-bonded partner, His. This proton-coupled electron transfer process in photosynthesis has inspired the preparation of artificial redox relays comprising different benzimidazole-phenol dyads. When the substituents are strong proton acceptors such as amines (Figure 1), theory predicts that a concerted two proton transfer process associated with the electrochemical oxidation of the phenol will take place. Also, theory predicts a reduction in the redox potential of the phenol by ~300 mV and a small kinetic isotope effect (KIE). Indeed, electrochemical (CV), spectroelectrochemical (IRSEC), and KIE experimental data are consistent with these predictions. The E2PT process shown in Figure 1 results in the translocation of protons over a distance of ca. 7 Å and is a starting point for the design of bioinspired proton wires [1].

The EPT process could be light-driven [2]. For that purpose, the porphyrin-BIP dyads were prepared (Figure 2). The excited singlet state of the porphyrin (lifetime ~10 ns) is quenched to ~270 ps in **4OH-PF$_{15}$** and to only 2 ns in **2OH-PF$_{15}$**, in acetonitrile. The quenching is solvent polarity dependent and can be assigned to the electron transfer from the phenol to the excited state of the porphyrin. However, the resulting charge separated state has not been detected due to inverted kinetics, i.e., it recombines faster than it is formed. Strategies to increase its lifetime include substituting the BIP moiety (Figure 2) with CH_2NEt_2, so that an E2PT process can occur.

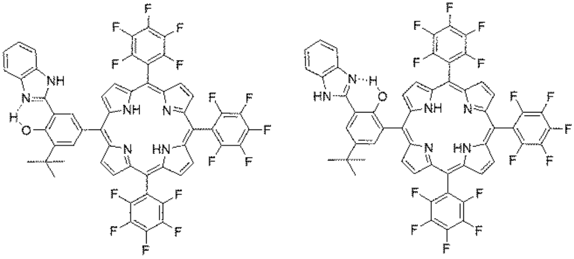
4OH-PF$_{15}$ 2OH-PF$_{15}$

Figure 2

The rational design of these systems has implications for managing proton activity at catalytic sites for redox-based energy conversion and may provide a better understanding of coupled systems for proton motive force generation in living cells.

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FLASH TALKS

FT1- Amoxicillin coated gold nanoparticles with photo-antibacterial action on antibiotic resistant strains

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Novel antibacterial strategies are badly needed as a consequence of the growing resistance of bacteria to conventional antibiotics. Photodynamic Antibacterial Chemotherapy (PACT) has recently proved to be an effective therapy when the photosensitizer presents selectivity for prokaryotic cells [1] . In fact, in the present work, gold nanoparticles were synthesized and stabilized with amoxicillin (amoxi@AuNP), which is a beta-lactamic antibiotic with high affinity for the bacterial wall. Amoxi@AuNP were prepared by 1-step synthesis at 50°C for 18 minutes. TEM revealed that the majority of the population is composed of nano-spheres (average 50 nm). However triangular and hexagonal micro-plates (50 to 90 nm) were also observed. The binding of amoxicillin (slightly modified) to the nanoparticle was confirmed through FT-IR and TGA. Importantly, the active site of the molecule, the beta-lactamic ring, was preserved intact [2]. The antibacterial activity of amoxi@AuNP against methicillin-sensitive *Staphylococcus aureus* ATCC 29213 (MSSA ATCC 29213) and methicillin-resistant clinical isolate of *Staphylococcus aureus* (MRSA 9455) was tested. Briefly, 100 µL of bacterial suspension (10^6 CFU/mL) and 100 µL of the tested solutions (37.5% PBS, 1.5 µg/mL amoxi@AuNP, 0.15 µg/mL amoxi@AuNP and amoxicillin at minimum inhibitory concentration (MIC): 2 µg/mL for MSSA and 32 µg/mL for MRSA) were mixed in a 96 wellplate. All samples were irradiated for a total of 90 min under white light (from blue, red and yellow LED combined) at 37 °C. An identical well plate was kept in the dark as a control. Aliquots of each samples were properly diluted and seeded on tryptic soy agar (TSA) plates for Colonies Forming Unit (CFU) counting. The 1.5 µg/mL amoxi@AuNP were able to inhibit bacterial growth of both MSSA and MRSA completely after just 30 min of irradiation. The same concentration of amoxi@AuNP was able to kill all the MSSA, but not the MRSA, after 90 min under dark conditions. This may be due to synergistic effect between the antibiotic and nanoparticles, because the amoxicillin itself was not bactericidal in this short period of time.

In summary, this study has demonstrated that PACT with amoxi@AuNP have an excellent potential in treatment of infectious diseases. Additionally, our group have reported their high biocompatibility and non-toxic properties to the host [3]. Further research would include evaluation of their effects in biofilms.

FT2- Photochemical formation of a fluorescent thymidine-pterin adduct in DNA

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Most solar radiation incident on the surface of Earth in the UV-range corresponds to wavelenghts between 320 - 400 nm (UV-A). This fraction of radiation is poorly absorbed by the DNA biomacromolecule, and therefore it is responsible for only low amounts of directly formed photolesions. Nevertheless, UV-A radiation acts indirectly by photosensitized reactions and is recognized as a class I carcinogen [1]. A photosensitized reaction is a photochemical modification occurring in a molecular entity as a result of the initial absorption of radiation by a photosensitizer [2]. Pterins belong to a family of heterocyclic compounds present in a wide range of living systems and participate in relevant biological functions. Under UV-A excitation, pterins can fluoresce, undergo photooxidation and generate reactive oxygen species (ROS) [3]. In the presence of oxygen, pterin (Ptr) act as photosensitizer through type I (electron abstraction) and/or type II ($^1O_2$-mediated oxidation) mechanisms [4-5].

The photosensitized degradation of the pyrimidine nucleotide thymidine 5'-monophosphate (dTMP) by Ptr under anaerobic conditions generates an adduct, where the pterinic moiety is attached to the nucleobase. The spectroscopic properties of the adduct are similar to those of Ptr itself [6].

The main objective of this work was to test the photodegradation of an oligonucleotide chain in the presence of Ptr and UV-A. Single stranded oligonucleotide of dTMP with the sequence 5´-d(TTTTT)-3´ (dT_5) was exposed to UV-A radiation in the presence of Ptr in neutral aqueous solutions at room temperature, under different experimental conditions. The samples were analyzed by UV-Vis spectrophotometry, HPLC coupled to a photodiode array and fluorescence detector and UPLC coupled to a mass spectrometry system.

Chromatographic peaks corresponding to both dT_5 and Ptr decreased with irradiation time. Several products presented absorbance in the UV-A region, and their absorption spectra showed a band centered approximately at 340 nm, which is similar to the typical low-energy band of Ptr. Moreover, some of these products were fluorescent and emitted at 450 nm when excited at 350 nm, which is compatible with the emission properties of Ptr. Products were analyzed by mass spectrometry, and the mass spectra showed a group of signals with *m/z* 808.65, which correspond to a di-charged ion of a compound bearing both of the photosensitizer and the oligonucleotide moieties. Thus, a covalent bond between Ptr and dT_5 occurs in anaerobic conditions.

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FT3- Variability in chlorophyll fluorescence spectra of Eggplant Fruit grown under different light environments: case study

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The main goal of the present work was to clarify physiological strategies in plants whose chloroplasts were developed under different light environments. The specific objective was to elucidate the influence of the spectral distribution of light on the chlorophyll fluorescence ratio and on photosynthetic parameters. To achieve this purpose, three species of Eggplant fruit (black, purple and white striped and white) were used as case study and their chlorophyll fluorescence was analyzed in detail. Spectra of the non-variable fluorescence in each part of the fruit were corrected for distortions by light reabsorption processes using a physical model. The main conclusion of this work was that the corrected fluorescence ratio depended on the contribution of each photosystem to the fluorescence and consequently on the environmental lighting conditions, becoming higher when illumination was rich in long wavelengths. Variable chlorophyll fluorescence, similar to that observed from plant leaves, was detected for the pulp of black eggplant, for the pulp of purple and white striped eggplant and for the intact fruit of black eggplant. The maximum quantum efficiency of photosystem II in the light-adapted state (Fv´/Fm´), the quantum efficiency of photosystem II (ΦPSII), and the photochemical and non-photochemical quenching coefficients (qP and qNP/NPQ respectively) were determined in each case. The results could be explained very interestingly, in relation with the proportion of exciting light reaching each photosystem (I and II). The photochemical parameters obtained from variable chlorophyll fluorescence, allowed monitoring non-destructively the physiological state of the black fruit during storage for both chilled or room-temperature conditions.

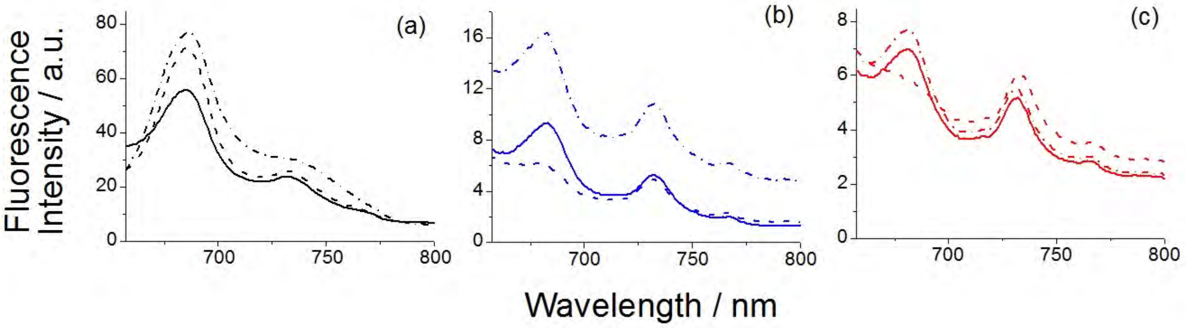

Figure 1: Fluorescence spectra corrected for the detector response (Fo) and additionally corrected for light re-absorption processes for the different parts of black eggplant (a),purple and white striped eggplant (b) and white eggplant (c). Whole fruit (—), peel (---)and pulp (- ・ -).

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FT4- Effects of Gold Nanoparticles on the photophysical parameters and photosynthetic capacity of Leaves and Chloroplasts

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When light impinges on a leaf, part of it is reflected, another part is transmitted and a third fraction is absorbed by the pigments and transferred to chlorophyll-a. Excess energy of excited chlorophyll-a can initiate the process of photosynthesis, be dissipated as heat or be emitted as fluorescence. As these three processes are competitive, chlorophyll fluorescence analysis gives information on changes in photosynthetic efficiency and heat dissipation [1].

Due to the spectroscopic characteristics of the gold nanoparticles (AuNP), which absorb light in the visible, it was hypothesized that they could have a possible action on photosynthesis when interacting with plant material. Thus, in this work the variations of optical and spectroscopic properties of both leaves and isolated chloroplasts were studied in the presence of AuNP synthesized according to Diz (phDthesis) [2].

Leaves of *Robiniapseudoacacia* were immersed in parallel in a AuNP suspension (17 nm in average diameter) and in a control solution. A significant decrease in the ratio of fluorescence maxima (Fred/Ffar-red) [3-4] was observed for the sample with AuNP relative to the control (reduction of 67% and 42% for excitation wavelengths 460nm and 520 nm respectively). Additionally, from pulse amplitude modulated (PAM) experiments, an augmentation in the photosynthetic parameters of leaves adapted to the light was detected: a 20% increase in the maximum photosynthesis yield (Fv/Fm' ratio) and a 30% increase in the quantum yield of photosystem II (ϕPSII).

Regarding studies on isolated chloroplasts of the same plant species, an analogous decrease in the Fred /Ffar-red relationship was observed in the sample with AuNP relative to the control. Measurements of the Hill Reaction showed an increase in the rate of reduction of the 2,6-dichlorophenolindophenol (DCPIP) probe, which is related with the maximum photosynthetic capacity, up to 280% for the sample with AuNP relative to the control (Figure 1). Preliminary studies of the maximum rate of oxygen production also showed that it doubled in samples containing AuNP.

Changes in the Fred/Ffar-red ratio are usually associated with stress either in the leaf or in chloroplasts. Nevertheless, in the presence of gold nanoparticles, the increase in the rate of reduction of DCPIP as well as in the rate of evolution of oxygen for chloroplasts and the increase of photosynthetic parameters from PAM measurements for leaves could indicate a striking increase in the photosynthetic capacity of the plant material.

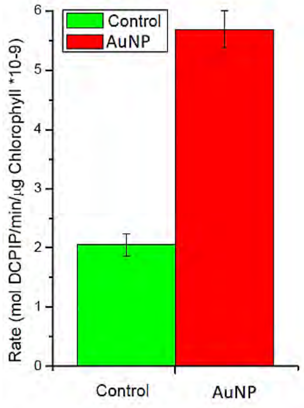

Figure 1: Rates of reduction of DCPIP in isolated Chloroplasts.

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FT5- “SNORKELLING” *vs* “DIVING” IN MIXED MICELLES PROBED BY MEANS OF A PHOTOACTIVE BATHYMETER

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Time-resolved spectroscopy, redox chemistry, bile salts, cholesterol

Bile salts/mixed micelles (MM) play an essential role in keeping material substances such as, for instance, cholesterol at the appropriate concentrations in solution. In addition, the introduction of MM in pharmaceutical formulations as a vehicle for drugs that are not soluble in water has eliminated many disadvantages associated with using other non-aqueous solvents.[1] The efficient encapsulation of drugs such as (S)-naproxen into MM has been stablished by time-resolved fluorescence and laser flash photolysis.[2]

In the present work, we have designed a photoactive bathymeter able to report on the increasing depth of encapsulated molecules in MM. To achieve this goal, the built photoactive bathymeter is based on a carboxylic acid tail end, to ensure floating on the MM surface, and a signalling methoxynaphthalene (MNP) chromophore at a fixed distance, to reveal “snorkelling” *versus* “diving” inside MM.

Information about the minimum distance the fluorophore “dives” to achieve protection from iodide anions in aqueous phase is investigated by time-resolved fluorescence. The photoactive bathymeter concept has been applied to other set of compounds containing the MNP.

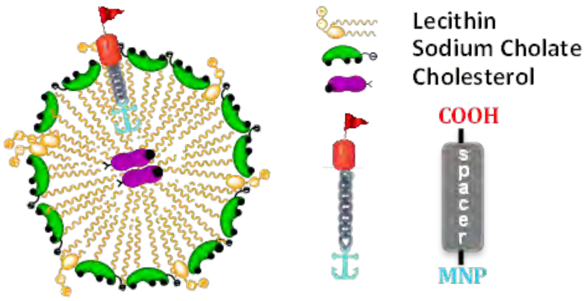

Figure 1: Cartoon representation of the photoactive probes with different spacer lengths anchored to the surface by the acid while keeping the chromophore diving as far as allowed inside MM.

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FT6- Photophysical, photochemical and photosensitizing properties of a Rhenium complex with dipyrido[3,2-a:2,3-c]phenazine (dppz) and norharmane (nHo) as ligands, $Re(CO)_3(dppz)(nHo)^+$. A Laser Flash Photolysis study

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The formation of adducts between complexes of Re(I) and biological macro-molecules such as DNA has been a subject of considerable interest, mainly because of the potential biomedical and/or biotechnological applications [1], among others. In this types of adducts, cationic transition metal complexes strongly interact with the negatively charged DNA backbone (i.e., phosphate groups). The intrinsic environment-sensitive photophysical and photochemical properties of Re(I) complexes make them suitable as DNA probes and/or Type I-photosenzitizers [2].

In this work we present a laser-flash photolysis characterization of the transient states involved when a novel Re(I)-complex, $Re(CO)_3(dppz)(nHo)^+$ (with *9H-Pyrido[3,4-b]indole* or nHo and *dipyrido[3,2-a:2,3-c]phenazine* or dppz as ligands) is subject to irradiation photoexcitation (at 351 nm). Briefly, in neat MeOH, laser pulses induce the formation of a transient with $\lambda_{max} = 460$ nm, assigned to the dppz triplet state, ^{3}IL. The transient absorbance decay was monoexponential with a $\tau = 3.54$ µs. In pure H_2O, this state is shutdown and, in consequence, the formation of such a transient was not observed. The interaction of photo-excited $Re(CO)_3(dppz)(nHo)^+$ with calf-thymus DNA (DNA_{ct}) was also investigated. Results show that, upon DNA_{ct} addition to the aqueous solution, and subsequent laser irradiations an absorbance transient is observed, centered also at $\lambda_{max} = 460$ nm. The contrast between the photobehavior of $[Re(CO)_3(dppz)(nHo)]^+$ when subject to irradiation in the absence and in the presence of DNA suggests a distinctive micro-environment for the investigated complex. The latter observation might be accounted for the well-known intercalative properties of dppz ligand. Therefore, the intercalation of $[Re(CO)_3(dppz)(nHo)]^+$ in the DNA_{ct} double-helix would provide a hydrophobic environment to the complex.

In addition, TEA (an electron donor) and MV^{+2} (an electron acceptor) were used as scavengers to further ascertain wheter the $^3MLCT_{Re\rightarrow dppz}$, $^3MLCT_{Re\rightarrow nHo}$ and/or ^{3}IL excited states of the intercalated $[Re(CO)_3(dppz)(nHo)]^+$ have a role in the photoredox procceses.

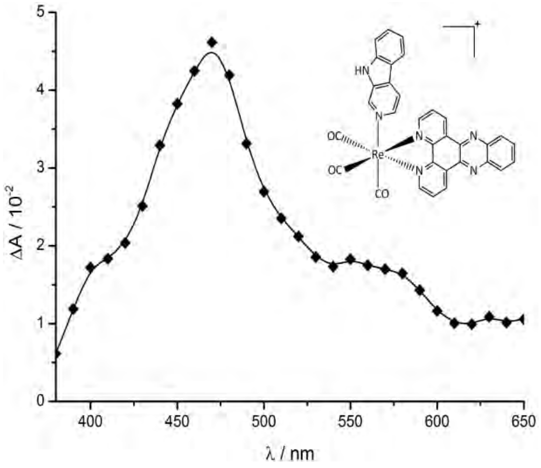

Figure 1: Flash photolysis spectrum of $Re(CO)_3(dppz)(nHo)^+$ in methanol. *Inset*: chemical structure of the complex.

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FT7- Charge Distribution-Inactivation Relationships of Chlorine Derivatives in Photoinactivation of *S. aureus* and *E. coli*

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The treatment and eradication of infections produced by microorganisms have become extremely difficult to achieve due to the wide variety of microbial resistance mechanism. This fact has focused the application of photodynamic inactivation (PDI) as a new effective treatment. This one is based on the administration of a photosensitizer which is preferably accumulated in microbial cells; subsequent irradiation with visible light in the presence of oxygen, generates reactive oxygen species (ROS) that produce a cascade of biochemical events causing the destruction of pathogens microorganisms. Chlorins are effective, safe and strong candidates as photosensitizer because they present high quantum yield of singlet oxygen and intense absorption band between 650-670 nm, wavelengths were the biological tissues are transparent to light.

In this work, we reported the synthesis of two new chlorines derivatives ($TPCF_{16}$-NMe_2 and $TPCF_{16}^{5+}$), which contain four 4-(2-*N*,*N*-dimethylaminoethoxy)phenyl groups and 4-(*N*-buthyl-*N*,*N*-dimethylamino)phenyl groups at the *meso* position of the macrocycle, respectively. Moreover, $TPCF_{16}^{5+}$ is a pentacationic chlorine, while $TPCF_{16}$-NMe_2 does not possess intrinsic charges and the tertiary amines are charged at physiologic pH.

The ability to produce singlet molecular oxygen was determined by the decomposition of 9,10-dimethylanthracene, obtaining quantum yields higher than 0.2 for both chlorins. Also, the formation of superoxide anion radical was detected in the presence of both photosensitizers.

In vitro experiments showed that both chlorins were rapidly bound to microbial cells at short incubation periods. In PDI treatment, 30 min irradiation and 5 μM $TPCF_{16}^{5+}$ was required to produce 7 log reduction of *S. aureus* cells viability whereas 15 min irradiation and 0.5 μM $TPCF_{16}$-NMe_2 was required to achieve the same effect. On the other hand, $TPCF_{16}^{5+}$ do not produce effect on *E. coli* cells after 30 min of irradiation and 5 μM photosensitizer, in contrast to $TPCF_{16}$-NMe_2 that produces 99.9999% of cellular inactivation at the same time of irradiation but with a much lower concentration. $TPCF_{16}$-NMe_2 was highly effective for the eradication of both, Gram positive and Gram negative bacteria. In summary, this work reveals that $TPCF_{16}$-NMe_2 has potential to be applying in PDI of bacteria cells and disclose that the charge distribution plays a key role in the design of effective phototherapeutic agents.

FT8- Modeling chlorophyll fluorescence at canopy level for different species

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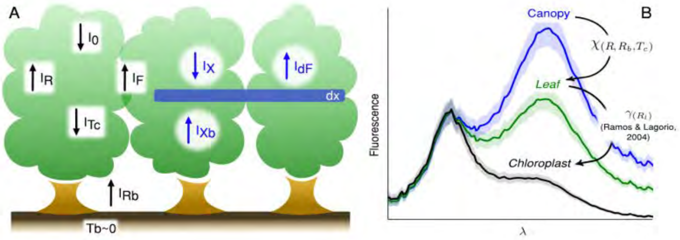
Chlorophyll fluorescence is used as an indicator physiological state of plants. Remote acquisition of fluorescence allows the diagnosis of large field extensions, even from satellite measurements [1]. However, fluorescence emerging from chloroplasts, the one directly connected to plant physiology, undergoes reabsorption proccesses both inside the leaf and the canopy, which completely distort the observed emission spectra [2,3]. Therefore, to draw accurate inferences about plant health, it is necessary to correct the observed canopy fluorescence taking into account these two reabsorption proccesses [4]. In a previous work, we have shown the theoretical development and experimental validation of a biophysical model that allows retrieving leaf fluorescence from that of the canopy using a correction factor which is a function of canopy and soil reflectance and canopy transmittance [5].

In this work, we apply our fluorescence correction model to canopies of different species and, mainly, different canopy structures. Plants used were: ficus (*Ficus benjamina*, planophile), maize (*Zea mays*, erectophile), oats (*Avena sativa*, erectophile), pea (*Pisum Sativum*, planophile) and ryegrass (*Lolium multiflorum*, erectophile). Canopy and leaf fluorescence spectra were registered for each species and corrected canopy fluorescence spectra were obtained and compared with the leaf spectra. The model showed a higher accuracy at predicting leaf spectra of planophile plant covers than of erectophile ones. Moreover, a reasonable dependence on the amount of biomass was found. The performance of the fluorescence reabsorption model will be discussed in terms of the photophysical assumptions and model equations.



(A) Canopy photophysical model, with photon fluxes taken into account by the model.
(B) Chlorophyll fluorescence corrected from canopy to chloroplasts.

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FT9-Fluoroquinolone Antibiotics Encapsulation in Calcium Phosphate-Nanoliposome for Bacteria Treatment

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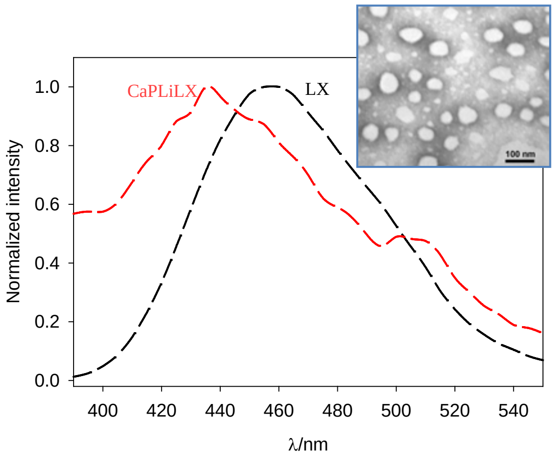
Liposomes are self-assembly structures of natural phospholipids which have been under study as drug delivery systems mainly due to their high biocompatibility in terms of composition, size and physicochemical properties [1]. Despite of the fact liposomes are promising for biomedical applications; one of the drawbacks inherent to their structural assembling is the leaking of entrapped molecules before reaching their target. Moreover, the liposomes tendency to coalesce reduces their stability in suspension and the targeting efficiency [2]. As well, the interaction with membranes and biological fluids provokes mechanical stress on liposomes. The coating of liposomes with biocompatible and biodegradable materials as calcium phosphates (CaP) [3,4] brings stability, rigidity and biocompatibility prolonging the circulation time in biological media. Fluoroquinolones (FQ) are synthetic antibiotics with a broad action against pathogens like *Staphylococcus aureus, Streptococcus pneumoniae, Pseudomonas aeruginosa, Escherichia coli, etc* [5]. The search for a nanostructured system that protects the FQ from external effects and delivers antibiotics in the vicinity of pathogens is fundamental to diminish the problems associated with their susceptibility in biological media.

In this work we developed a nanovehicle based on 1,2-dioleoyl-sn-glycero-3-phosphate (DOPA) liposomes with a CaP-coating which encapsulate fluoroquinolone drugs, levofloxacin (LX) or ciprofloxacin (CX) (named CaPLiLX and CaPLiCX, respectively), for their use as antibiotic controlled delivery devices. The size and shape of the nanoliposomes and effect of CaP-coating on the stability was evaluated through electronic microscopy techniques and electrophoretic mobility measurements. The incorporation of FQ in the nanovehicles was investigated using the characteristic emission peaks and emission lifetimes of the drugs. The growth inhibition of bacterials smears of *S. aureus* was studied in the presence of nanovehicles.



Coated- liposomes with diameters bellow 100 nm were succesfully obtaneid (see inset in the figure). The emission maxima of the antibiotics encapsulated in coated nanoliposomes (see main figure for LX) present a blue shift compared to the corresponding drugs in phosphate buffer solution (PBS, pH 7.4). The result supports the incorporation of LX and CX in the nanoliposomes.

The fluorescence decay of LX and CX 6μM in PBS solutions was well fitted to a monoexponential function with fluorescence lifetime $\tau = 1.3$ ns for CX and $\tau = 6.2$ ns for LX which is in agreement with previous reported data. On the other hand, CaPLiLX and CaPLiCX traces were well-fitted to a tri-exponential decay function which include a < 1 ns lifetime attributed to the light scattering of the CaP-coated nanoliposomes. The second fluorescence lifetimes were assigned to drug aggregation and protonation in the liposome environment, which was also suggested from absorption spectra for both drugs. The third values were consistent with the increased lifetime for drugs molecules confined in hydrophobic environments.

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FT10- Photoreductions of Quinoxalin-2-one Derivatives.

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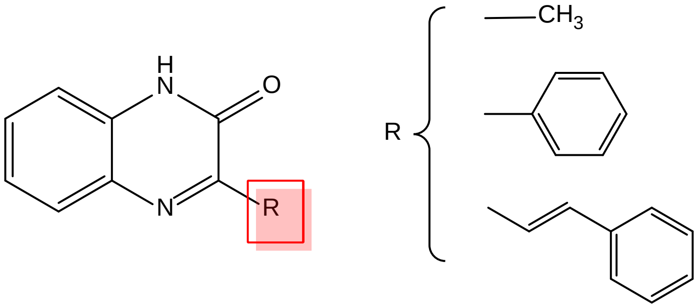
Quinoxalin-2-ones are scaffold of many compounds that present biological activity from antitumor to analgesic and some interesting photochemical reactions. 3- phenyl derivatives are photoreduced efficiently by amines by a stepwise transfer of electron-proton-electron, resulting in a metastable photoproduct that revert quantitatively to the starting quinoxalin-2-one [1,2] while 3-methyl derivatives gave stable annulation photoproducts when are photoreduced by *N*-phenylglycine, **NPG**, through a chain reaction reactions that follows a Hammett relationship depending on the substituent in the 3-methyl-quinoxalin-2-ones. [3,4] More recently, our attention have been focused in the study of 3-styryl photoreactions with **NPG** that generate several radical addition products and to the study of the strange behavior observed in the photoreactions of 3-phenyl derivatives with **NPG**.



We thanks FONDECYT Grant N° 1150567 for the financial support.

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FT11- Contributions of the Single-molecule Techniques to the Organic Tool-Kit: Click Chemistry as a Proof of Concept

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Pharmaceutical industry is continually seeking new avenues to develop drugs producing less toxic waste and by-products. Catalytic processes are normally improved through a trial-and-error approach, combined with the experience from decades of catalysis research. Although often successful, this approach essentially relies on chance. Alternatively, the rational design of new catalysts will lead to more efficient organic synthetic methods, thereby reducing waste, improving yield and safety. Single-molecule (SM) techniques are a powerful tool that can help organic chemistry at the bench. Knowledge on how a single molecule can reach a single-catalytic site, react and finally diffuse away brings useful information on the catalytic mechanism, the catalyst site composition and distribution, helping in the design of more effective catalysts. We present the first successful attempt to use catalysis studied at the single molecule-single catalytic site level to guide work at the bench scale, a strategy we refer as "*from the molecule to the mole*".[1] Thus, knowledge acquired at the molecular level is used to improve bench processes. Our group previously studied the performance of commercial Cu-on-charcoal catalyst (3% Cu) at the SM level where only 0.003% of the surface was active in a click reaction between alkynes and azides.[2]Although a very good catalyst, there is plenty of room for improvement. Inspired by SM results we developed a strategy to improve the catalytic activity at the bench scale, and back again to the SM we could rationalize improvements found at the bench.[3]

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FT12- A novel result about the stability of aqueous solution of folic acid under UV-A radiation

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Folic acid or pteroyl-L-glutamic acid (PteGlu), a synthetic and oxidized form of folate, is a pterin derivative widespread in biological systems, whose chemical structure is composed of three moieties: a 6-methylpterin, a p-aminobenzoic acid (PABA), and a glutamic acid (Glu) residue [1]. PteGlu is a precursor of coenzymes involved in the metabolism of nucleotides and amino acids. It plays an important role in the prevention of a number of important health complications such as male infertility, neural tube defects (NTD) in the developing foetus and some cancers [1]. Different studies have suggested that photolysis of PteGlu lead to increased risk of NTD, and that skin pigmentation is an effective mechanism of protection against folate depletion.

Many reports have studied the photodegradation of aqueous solutions of PteGlu under UV-A radiation. Nevertheless, no one has investigated the influence of the presence of pterins impurities on the photostability of PteGlu. In order to study this, air equilibrated acidic aqueous solutions of purified PteGlu (pH 6.0±0.1), were irradiated under UV-A radiation (350 nm) for different periods of time. The samples were analyzed by UV-vis spectrophotometry and High Perfomance Liquid Cromatography photodiode (HPLC-PDA) and fluorescence (HPLC-RF) array detectors. The results were compared with those obtained from solutions of unpurified PteGlu from different commercial solids.

In order to characterize the impurities present in the commercial sample of PteGlu (Schircks Laboratories; purity > 98.5%), an acid aqueous solution was prepared in the absence of light and was analyzed by HPLC and HPLC coupled to a Mass Spectrometry detector (HPLC-MS). The analysis using the HPLC-PDA detector showed a chromatogram with only one peak which corresponds to PteGlu. However, fluorescence chromatogram obtained by HPLC-FL analysis showed new peaks, suggesting that another compounds are present in the sample. The spectral features of the impurities are similar to those reported for PABA-Glu, 6-carboxypterin (Cap) and 6-formylpterin (Fop), and the presence of these compounds was confirmed using the corresponding standard. The amount of each impurity was determined by integration of each peak in the fluorescence chromatograms using the calibration curves of each compound.

A Synergi Polar-RP column (ether-linked phenyl phase with polar endcapping, 150 x 4.6 mm, 4 ⍰m, Phenomenex) was used for isolation of PteGlu from HPLC runs (preparative HPLC), by collecting the mobile phase after passing though the RF detector. Solutions containing 100 % NH_4Ac (1 mM, pH 6.5 ± 0.1) were used as mobile phase. The same column and runs conditions were used to analyze the purity of the isolated PteGlu sample. The analysis of the collected fraction suggested that the isolation of PteGlu reduced significantly the amount of each impurities present in the sample.

Air equilibrated acidic aqueous solutions of purified PteGlu were irradiated under UV-A radiation for different periods of time and the samples were analyzed by HPLC. The results were compared with those obtained from an unpurified solution. The results indicated that the rate of photooxidation of purified PteGlu decreased significantly in comparison with the unpurified compound. PteGlu was rapidly oxidized into Fop and PABA-Glu when the percentage of pterins impurities increases. This result surprisingly suggests that the photodegradation of PteGlu could be due to the presence of impurities and not due to its photooxidation itself.

Acknowledgements

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FT13- Protein association dynamics studied by super resolution fluorescence microscopy

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Fluorescence nanoscopy render molecular localization within a precision of tens of nanometers, 10-50 times lower than the diffraction limit. This possibility opens the way to study molecular co localization or association between species in the intermediate range between FRET (1-10 nm) and conventional confocal microscopy (hundreds of nanometers), provided the target species can be distinguished by their fluorescent marker.

The quantitative analysis of the colocalization distribution of two emitting species was approached in many ways: cluster density in color scale, cluster analysis, spatial correlation function and comparison with regular patterns.

In this work, we analyze the application of distribution functions to quantify the extent of molecular association in one and two color Stochastic Optical Reconstruction Microscopy (STORM) image sets. From molecular localization maps we obtain the first neighbor distance (dFN) between molecules of the same (A-A and B-B) and of different species (A-B and B-A). We build the complementary cumulative distribution function (CCDF) of dFN in each case. The analysis and comparison of these four CCDF can distinguish between: 1) association and distribution in a two dimensional compartment, 2) a one dimensional environment (membrane or filament), 3) a 1:1 association or 4) a clustering of one type of molecules around the other.

We apply this methodology to the analysis of the influence of RSUME (RWD-domain-containing sumoylation enhancer) on the dynamics of the HIF-VHL (Hypoxia-inducible factor, von Hippel Lindau) complex. To this aim, in a set of experiments carried out under identical conditions, we mark the proteins pairwise with two different rhodamine dyes by the postraductional modifications known as SNAP-CLIP. Localization is performed at the single molecule level by two-color STORM experiments.

We demonstrate that the dyes are adequate for these type of experiments and analyze the cellular distribution of proteins by comparing the actual distribution with simulated random and associated distributions performed in the same location pattern.

FT14- Nanoemulsions of *Trichocline sinuata* (Asteraceae) extracts as sunlight-activated insecticides

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Despite of the recent major advances in photherapy drugs, natural products are known to be the main source of new phototoxic molecules [1]. Since the potential of the midwestern Argentinian flora remains unexplored, isolating new photactive compounds or plant extracts from this region may provide boudless opportunities to obtain insecticides with high phototoxic potential [2]. Chagas-Mazza disease is the only endemic vector-borne disease of epidemiological importance in Argentina due to its high prevalence rate [3]. Chagas-Mazza disease is caused by the protozoan parasite *Trypanosoma cruzi*, and human infection results mainly from the contamination of vulnerable surfaces with the feces of an infected *Triatoma infestans* bug known as *winchuka* or *vinchuca* in Argentina. Natural compounds, such as coumarins, thiophenes, hypercin and chlorophyll [4] can act against a variety of noxious insects [5]. When these compounds are activated by light at specific wavelengths, they convert triplet oxygen ($^3O_2$) into singlet oxygen ($O_2(^1\Delta_g)$), which is a very strong oxidant. Nanoemulsios are applied to enhance the solubility, transparence and bioavailability of hydrophobic compounds. Dispersions of oil and water stabilized by an interfacial film of surfactant molecules with a droplet size < 200 nm have higher solubilization capacity and their thermodynamic stability offers advantages over unstable dispersions. Emulsions and dispersions can be manufactured with little energy input and have a long shelf life. These nano-sized droplets are generated by ultrasonic cavitation, leading to an enormous increase in the interfacial areas, which would influence transport properties [6]. In order to evaluate the ability of *Trichocline* sinuata ("árnica del campo") DMC extract nanoemulsions (DCMNE) as photoinsecticide facing Triatoma infestans, profiles of DCM extracts were developed employing spectroscopy and chromatographic technics. All extracts present the same UV spectra resembling furanocoumarin compound (maximum absorbance at 309, 267 and 247 nm). Using standard compounds, for HPLC-DAD we determined that extracts were made of three majority furanocoumarins: xantotoxin, bergapten and trichoclin. The minority extract composition was determined employing CG-Ms (finger print), finding a great number of furanocoumarins, such as dihidroxitrichoclin, psoralene, isopipinellin and other phototoxic compound like angelicin. Nanoemulsions were then dispersed over 30 nymphs of 4 º stages with microapplicator, and the nymphs subsequently placed in closed containers exposed to sunlight. Mortality was recorded every 24 hours up to 72 hours. *The results revealed a mortality rate of 50% for DCMNE of T. sinuate.* To determine the photodynamic mechanism by which DCMNE acts as photoinsecticide, we measured the production of reactive oxygen species. The photo-oxidation of L-tryptophan (Trp) was studied following the decrease of the fluorescence intensity at 355 nm for generation of singlet oxygen $O_2(^1\Delta_g)$. The production of Superoxide radical ($O_2^{\cdot -}$) was assessed by employing UVA-light irradiated nitroblue tetrazolium (NBT), and their absorbance measured at 560 nm. This considerable body of data allowed us to conclude that DCM-NE of T. sinuata acts as photoinsecticide against *Triatoma infestans*.

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FT15- Fluorescence of highly absorbing samples in transmission geometry with a commercial spectrofluorometer

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The experimental adquisition of emission spectra and quantum yields under highly absorbing conditions generally represents a difficult task due to the presence of internal filter effects. In this sense, we have recently developed a simplified methodology to obtain: a) steady-state emission spectra and b) fluorescence quantum yields (Φ_F) of samples with high optical density at both excitation and emission wavelengths.[1] The experimental configuration consists of a commercial spectrofluorometer adapted to a transmission geometry, where the detection of emitted light is performed at 180° with respect to the excitation beam. The main goal of this approach is the use of short path-lengths ensuring small excitation and detection volumes, in order to guarantee overlaped excitation and detection regions for all optical densities. The procedure includes two different mathematical approaches to describe and reproduce distortions caused by reabsorption in both emission spectra and quantum yields.

In this work we will discuss three different application cases for which our metodology is useful: a) 9,10-diphenylanthracene (DPA) in toluene, b) quinine bisulphate (QBS) in sulphuric acid and c) the ionic liquid p-toluensulfonate of 1-butil-3-metilimidazolium (BMIMTOS).

a) DPA in toluene was studied in a concentration range from 1×10^{-5} M to 1×10^{-2} M. This dye was selected to validate our methodology since it presents significant resorption and re-emission in concentrated solutions without self-quenching or aggregation phenomena. From the fluorescence intensity at 460 nm, where reabsorption is negligible, we obtained $\Phi_F \approx 1$ for the entire concentration range. On the other hand, Φ_F values, calculated from the integrated emission spectra, decrease as the concentration increases. We will show how this effect, caused by reabsorption, can be quantitatively described by the two mathematical approaches.[1]

b) QBS in sulphuric acid was estudied in a concentration range from 1×10^{-5} M to 1×10^{-2} M.[1] This dye was selected to demonstrate that our methodology also constitutes a very simple and robust alternative to determine self-quenching constants, K_{SQ}. QBS shows no aggregation and a large stokes-shift that prevents, in principle, reabsorption and re-emission events in concentrated solutions. However, the re-absorption of 6% observed in our experiments confirms that it is necessary to perform appropriated corrections on emission spectra for the accurate data processing. The value obtained after corrections, $K_{SQ}=18.4 \pm 0.1\ M^{-1}$, shows no significant differences with those obtained from steady-state and average lifetimes by other authors, pointing out the diffusional nature of the self-quenching phenomenon.[2]

c) BMIMTOS constitutes a novel kind of fluorescent ionic room-temperature fluid medium showing a high density of fluorophores. For this reason, our metodology constitutes a valuable tool to evaluate the photophysics of this compound. We observed that the fluorescence of BMIMTOS enhances about 300% when temperature falls from 55 to 0ºC. The increment is associated to excimer formation and strongly differs to those observed for toluene in the same temperature range.

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FT16- Exploring MS and IRMPD fingerprints of protonated Watson-Crick and Hoogsteen pairs of (Cytosine-Guanine)H$^+$

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One decade after Watson and Crick (WC) discovered the double-helix structure of DNA [1], Hoogsteen (Hoo) [2] reported a crystal structure in which the base pair had a different geometry to that reported by WC. While WC isomers are considered as the canonical paring forms in DNA transporting the genetic information, Hoo isomers are associated to the formation of triplex related to several human diseases [3]. Therefore, the development of simple techniques that allow identifying the existence of WC or Hoo isomers is of a broad interest.

In this we report a method to prepare the protonated Cytosine-Guanine (CGH$^+$) pair in solution, either in the WC or Hoo isomeric structures that retain their structure after been transferred to the gas phase by Electro Spray Ionization (ESI) where their finger prints are characterized by mass spectrometry (MS) in an 7T FT-ICR Bruker Apex Qe mass spectrometer and by infrared multiphoton dissociation (IRMPD) spectroscopy with the Free-Electron-Laser (FEL) at CLIO (Centre Laser Infrarouge d´Orsay). Calculations at the DFT level are performed to help the interpretation of the experimental results.

Briefly, the mass fragmentation pattern as well as the IRMPD spectra of the parent ion m/z = 263 (CGH$^+$), strongly depends on the pH of the solution (Figure 1), indicating that different isomers are produced. Therefore, the protonated CGH$^+$ WC or Hoo isomers can be selectively prepared in the solution and this structure is preserved upon vaporization in an ESI source. The MS and IRMPD fingerprints of each isomer allow to unequivocally assign them. This is expected to be applicable as an easy methodology based on MS and/or IRMPD to determine the existence of Hoo pairs associated to diseases and mutations, in real samples.

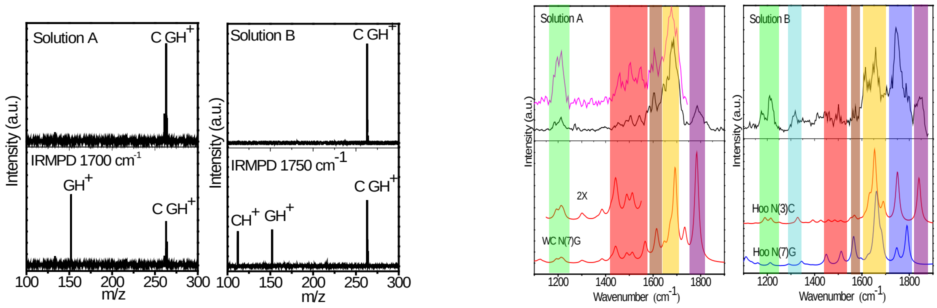

Figure 1: Left: MS of isolated CGH$^+$ protonated pair before fragmentation (upper panel) produced from solution A (pH=5.8) and solution B (pH=3.5) and after fragmentation by IRMPD (lower panel) at 1700 cm^{-1} (left) and 1750 cm^{-1} (right).

Rigth: IRMPD spectra of the parent ion CGH$^+$ (m/z = 263) (upper panel) produced by solution A and solution B). The lower

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Abstracts of Posters Presentations

P1-Role of Electrolytes in Natural Dye Sensitized Solar Cells

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In a global context of energy demand, dye-sensitized solar cells (DSCs) have emerged as an environmentally-friendly technology to the electricity generation through solar energy conversion, mainly due to their simple design and affordable production cost [1]. Sensitizing dyes are the components of DSCs responsible for absorbing visible light efficiently. Synthetic dyes of different classes, such as metallic complexes, porphyrins and organic molecules, exhibit the best conversion efficiencies. However, despite lower efficiencies, the use of adequate natural dyes as DSC sensitizers is an advantage as a green alternative for being nontoxic, effortlessly obtained and easily prepared, with even lower production costs [1-2]. In this work, we analyzed the role of I^-/I_3^--based electrolytes with different solvents and/or additives in solar cells sensitized by extracts of mulberry (*Morus alba* L.), java plum (*Eugenia jambolana* Lam) and pomegranate (*Punica granatum*). For DSCs sensitized by mulberry, the change in the electrolyte solvent from acetonitrile/3-methyl-2-oxazolidinone (9:1 v/v) to acetonitrile/valeronitrile (85:15 v/v) leads to a significant upturn in Jsc, from 3.42 mA cm^{-2} to 4.14 mA cm^{-2}. This enhancement is possibly related to a decrease in the solvent viscosity and increase in its conductivity [2-3].

The use of pyridine in these electrolytes results in a considerable Jsc loss, as shown in Figure 1 ascribed to the anthocyanin's sensibility to the pH variation [4]. The presence of pyridine leads to a deprotonation of the anthocyanin with consequent desorption from the TiO_2 surface and, ultimately, to a decrease in the photon harvesting [4]. Therefore, pyridine-free electrolytes improves the efficiency of DSCs sensitized by anthocyanins.

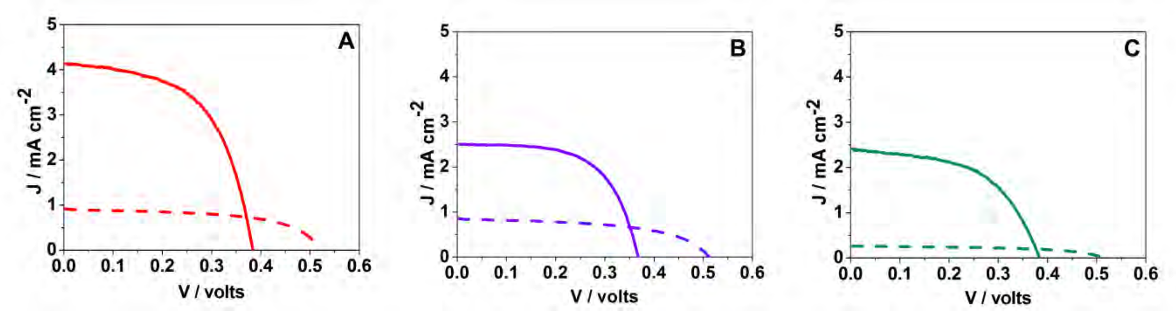

Figure 1. Current–voltage curves for DSCs sensitized by extracts (pH ~ 3) of mulberry (**A** - red), java plum (**B** - violet), and pomegranate (**C** - green) with an electrolyte constituted of I^-/I_3^- in acetronitrile-valeronitrile (85:15 v/v) without (—) and with pyridine (- - -) as an additive (~100 mW cm^{-2}, AM 1.5). (~100 mW cm^{-2}, AM 1.5).

In conclusion, the use of natural extracts in DSCs with an adequate electrolyte stands as an eco-friendly alternative to the energy generation and may lead to low-cost, low toxicity and easily-obtained devices.

Acknowledgements: FAPESP, CAPES and CNPq for financial support.

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P2-Photorearrangement of aryl benzoates in homogeneous and micro-heterogeneous media

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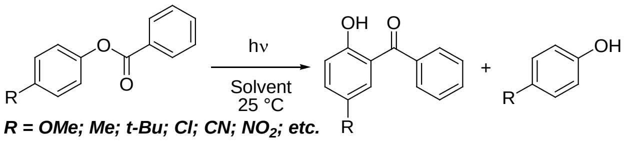
The photo-Fries rearrangement was discovered by Anderson and Reese in 1960[1] and the photophysical and photochemical aspects of the photoreaction have been studied.[2] The application of the photoreaction in organic synthesis has been also studied, for example, in the total synthesis of murrayacine, daunomicine and tetracyclines.[2] However, the photo-Fries rearrangement of aryl benzoates has been scarcely studied.[2] The photoreaction of aryl benzoates provides the preparation of 2'-hydroxybenzophenone derivatives that are used in solar creams, as possible actinometers and also, in the synthesis of building blocks of natural products. 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 homogeneous and heterogeneous media by means of steady-state and time-resolved spectroscopies. A representative series of *p*-substituted phenyl benzoates were prepared and fully characterized by physical and spectroscopical methods (pf, NMR). Preparative photochemical reaction led to isolate and fully characterized the benzophenone derivatives. Quantum yields of consumption (ϕ_r) were also measured in both media affording higher values of ϕ_r in heterogeneous than in homogeneous media. The constants of binding (K_b) were measured in presence of SDS (0.10 M) giving values between 70 and 1700 M^{-1} depending on the nature of the substituents. A high regio selectivity of the photoreaction was observed in heterogeneous media, favoring the exclusive formation of 2'-hydroxy benzophenones as the photoproducts. Laser flash photolysis (266 nm) of some representative esters in homogeneous media led to characterize the transients *p*-substituted phenoxyl radicals and adducts 2-benzoyl cyclohexadienones. These adducts finally evolve to 2-hydroxy benzophenone derivatives which are the main photoproducts of the photoreaction. Figure 1 shows the transient absorption and decay traces obtained for a solution of *p*-methoxyphenyl benzoate in SDS 0.10 M.

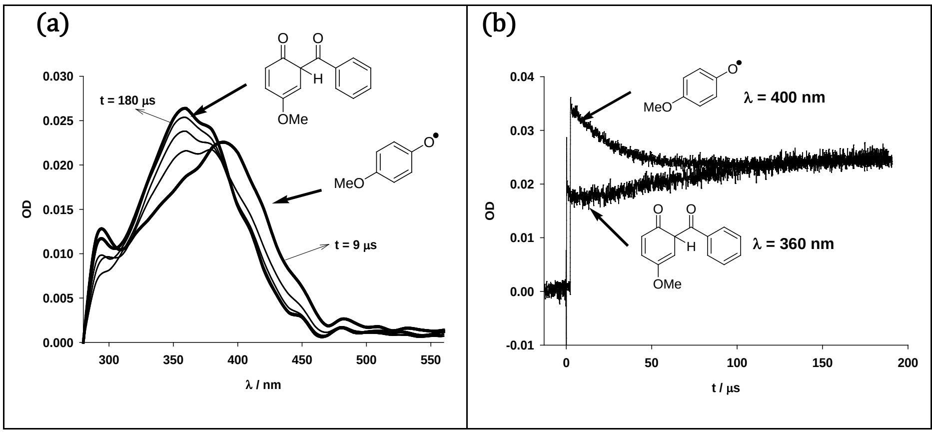


Figure 1. Transient absorption and decay traces of a solution of *p*-methoxyphenyl benzoate.

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P3- Inactivation of *Pseudomonas aeruginosa* by synergistic effects of ofloxacin and photodynamic treatment

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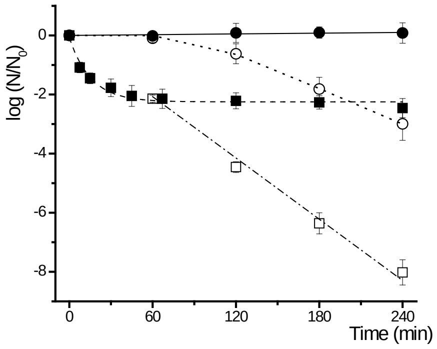
In a recent study concerning the effects of MB (methylene blue) and light on *P. aeruginosa*, a minority bacterial subpopulation exhibiting increased ability to survive has been observed [1]. The response of this subpopulation to the treatment was similar to that of persister bacteria during exposure to antibiotics. This similarity, and a possible relationship between persistence and tolerance to oxidative stress [2], led us to suppose that a common mechanism could be reponsible for transient tolerance to photodynamic treatment and antibiotics. The initial objective of the present study was to test this hypothesis and, to do that, the antibiotic response of survivors to photodynamic treatment was assayed by challenging them with OFX (ofloxacin) immediately after the irradiation. Survival curves obtained with these cells were similar to those of the whole bacterial population, but unexpectedly colony formation was delayed. This observation suggests that damage produced by previous treatment hampers the growth of survivors to OFX, and led us to study the effectiveness of simultaneous application of MB light and OFX (Figure 1). Used alone the antibiotic reduced the bacterial population by 10^{-2} within 45-60 min, but further exposition had limited consequences on viability. The lethal effect of photodynamic treatment in the absence of OFX was undetectable during the first 30 min, and then reduced the population by $1/e$ (37%) in 22 min. By contrast, the loss of viability produced by MB and light in the presence of OFX started at the beginning of the irradiation, and the population was reduced by $1/e$ in 13 min. During the irradiations, survival fractions were reduced by 10^{-3} and 10^{-6} in the absence and presence of OFX, respectively.

These results do not support the existence of a mechanism allowing to tolerate both antibiotics and photosensitizers. If this mechanism exists, the cumulative effects overcome its influence. Conversely, the synergy observed here suggest that photodynamic therapy could be useful to reduce the number of persisters during treatment with antibiotics. This would improve the control of infections, since the effectiveness of an antibiotic could be limited by persister bacteria when the immune system of the host is unable to eliminate them [3].

Figure 1. Effect of simultaneous use of photodynamic inactivation and OFX. Bacterial suspensions ($5\ 10^{8}$ UFC/ml) were submitted to a protocol which include additon of OFX (95 μg/ml) at start time, addition of MB (15 μM) at 50 min, and irradiation (637 nm; 44 W m^{-2}) from 60 to 240 min. Controls were performed omitting the antibiotic, the photodynamic treatment or both. During the procedure, viable counts were obtained by plating or, when $\log(N/N_0) < -5.5$, by the membrane filter technique. Points represents the mean of 4 assays, bars represents standard deviations.



Symbol	Treatment	
	OFX	MB / light
●	-	-
○	-	+
■	+	-
□	+	+

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P4- Dityrosine: photochemical synthesis, isolation and characterization

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Oxidative damage to proteins leads to a variety of modifications which are markers of pathogenesis. One of the most important modifications is the dityrosine cross-link, an oxidative covalent bond between two tyrosine (Tyr) residues, which is known to occur in many diseases like amyloid fibril formation, Parkinson's disease and epidermoid carcinoma. The mechanism of dityrosine (Tyr_2) linkage starts with the one-electron oxidation of Tyr, which leads to the long-lived tyrosyl radical ($Tyr(\text{-}H)^•$). Two $Tyr(\text{-}H)^•$ are able to react yielding the Tyr_2. Radiation can induce the dimerization of Tyr by direct light absorption or by photosensitization process.[1] The cross-linking of free Tyr and tyrosyl groups in proteins was reported for reactions photosensitized by pterins derivatives,[2,3] a family of heterocyclic compounds which are present in a wide variety of living systems and participate in relevant biological functions.

Various attempts to synthesize Tyr_2 using different oxidizing agents were unsuccessful. However, oxidation of Tyr with peroxidase and hydrogen peroxide was shown to be the method of choice for *in vitro* production of Tyr_2.[4] The most important difficulty of this method is the isolation of pure Tyr_2 from the incubation mixture, which requires many steps. Despite of that, this method is still the main way to obtain Tyr_2 and although it has been improved, the purification step is still difficult. Taking into account the biomedical importance of Tyr_2, and the lack of studies on its properties due to the drawbacks of the synthesis and purification, the main aim of this work is to develop a new economic and simple method to prepare aqueous solutions of Tyr_2 with high purity. Our procedure is based on the dimerization of Tyr photosensitized by pterin (Ptr) in aqueous solutions under UV-A radiation. To develop this, air equilibrated acid aqueous solution of Tyr and Ptr were exposed to UV-A radiation at different concentrations of each reactant for different irradiation time. After the experimental conditions were optimized in order to produce the maximum amount of Tyr_2, the compound was isolated from HPLC runs by collecting the mobile phase after passing through the high perfomance liquid cromatography photodiode array (HPLC-PDA) detector. A C18 column was used for isolation of Tyr_2 and NH_4Ac 1 mM (pH 6.0) was used as eluent. The isolated fraction was analyzed by fluorescence spectroscopy, UPLC coupled to ESI mass spectrometry (UPLC-MS) and Proton Nuclear Magnetic Resonance (^{1}RMN). The mass chromatograms of isolated fraction showed a unique peak with a *m/z* value of 359.1239 Da which correspond to $[2Tyr\text{-}2H\text{-}H]^-$. In agreement with this, the mass chromatograms registered for the specific ion mass of 359.1239 Da showed that this molecular weight was observed at only one retention time, indicating that only one isomer of Tyr_2 is formed. The generation of this compound could be verified by means of its ^{1}RMN spectrum. The fluoresence quantum yield of the acid and basic forms were determined to be 0.25±0.03 and 0.46±0.07, respectively. The mass of Tyr_2 in the isolated sample was calculated taking into account the volume obtained during the isolation of the sample and its concentration. The result was compared to the initial mass of Tyr , and a value of 9 (±1) % was obtained for the overall yield of the process.

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P5- Reaction kinetics and mechanisms of degradation of organosilicon fungicide flusilazole

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Flusilazole is a triazole family fungicide. Because of its broad-spectrum of application, exhibits curative and preventive properties and is recommended for use in agriculture, horticulture and viticulture.

Hazard classification for flusilazole is class III, 'slightly hazardous' [1]. However, it is important to take into account, that indiscriminate use of pesticides, could lead accumulation in plants, foods, water reservoirs and food chain. Besides, some of them are resistant to the action of sunlight, temperature, water or microorganisms; resulting in high levels residues in plant tissue and environmental samples.

Sulphate and hydroxyl radicals are strong oxidants used in advanced oxidation processes (AOPs), like UV/ $S_2O_8^{2-}$, Fenton and the photo-assisted Fenton reaction (“photo-Fenton”). Those processes have attracted interest for the degradation of organic compounds in wastewater, including pesticides [2] [3].

Despite flusilazole is a widely used fungicide, documented data on their degradation mechanism and intermediate metabolites is lacking.

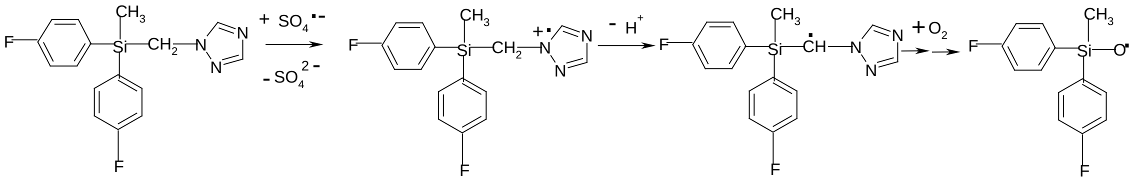
In the present work we investigated the kinetics and mechanism of the degradation of flusilazole initialed by $HO^{\bullet}$ and $SO_4^{\bullet -}$. These radicals were generated by laser flash photolysis ($\lambda_{exc.}$=266nm) of H_2O_2 and $Na_2S_2O_8$, respectively. Also, continuous-irradiation experiments were performed by “photo-Fenton” reaction of the fungicide with solar simulator and the nature of the primary degradation products formed were investigated by GC-MS analysis.

A possible degradation mechanism of the fungicide was proposed. To help identify the nature of the observed transients, time-dependent density functional theory (TD-DFT) calculations were employed.

By laser flash photolysis of $S_2O_8^{2-}$ with flusilazole, two absorbing intermediates were identified: the first transient absorbs at wavelengths of 300nm, and the second one has two maxima at 360 nm and 640 nm.

Using TD-DFT, intermediates were identified as a carbon centered radical (a structure) and siloxyl radicals Si—O$^{\bullet}$ (b structure).

In the continuous photolysis experiments, performed by photo-Fenton reaction of the fungicide, the main degradation product was silicic acid, diethyl bis(trimethylsilyl) ester. Silicon in the structure of flusilazole is fundamental for the generation of the intermediates proposed, which have in their structure Si-O-Si and Si-C bonds.



Flusilazole

a

b

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P6- Perfluorobutylation of *N*-oxide derivatives of pyridines, (*iso*)quinolines, and diazines through photoredox organocatalysis

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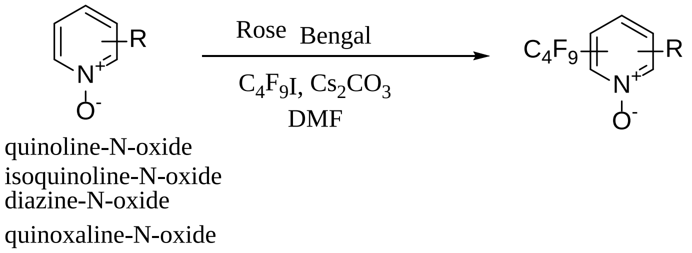
The perfluoroalkylation reactions of aromatic substrates are not as widespread and studied as trifluoromethylation methods. However, there are several reported protocols for substitution with perfluoroalkyl groups R_F which include those catalyzed by transition metals, through direct irradiation of perfluoroalkyl halides R_FX, and photoinduced electron transfer (PET) methods. On the other hand, there are very few examples that employ metal-free organic photocatalysts, such as commercial dyes, to produce R_F radicals, and no report on methods to achieve R_F substitution of *N*-oxide derivatives has been informed to date.

This presentation intends to explore a photoredox catalytic method with a commercial organic dye, Rose Bengal (RB), to generate R_F radicals which are shown to react with *N*-oxide derivatives of heterocyclic compounds giving rise to (hetero)aromatic *N*-oxide products substituted with R_F residues, according to the following general Scheme.



By irradiation with a conventional fluorescent lamp, the excited photocatalyst (i.e.: RB*) leads to a strongly reductant species capable of reducing *n*-C_4F_9I and generate the *n*-C_4F_9• radicals which in the process effect a homolytic aromatic substitution (HAS) on the (hetero)aromatic *N*-oxide compounds. The presence of Cs_2CO_3 becomes essential in order to regenerate the photocatalyst. The method studied herein does not require thermal chemical initiators to generate R_F radicals, nor short-wavelengths irradiation and is accomplished in the absence of transition metals. The yields of perfluoroalkylated products vary from very good to good. *N*-oxides with electron-withdrawing groups, afford low product yields. The position of the substituent is also important. Derivatives with methyl groups show low regioselectivity. Excellent quantitative yields are achieved with the isoquinoline-*N*-oxide as substrates. This is the first report on the direct perfluoroalkylation of *N*-oxide derivatives.

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P7-Photochemistry and Photophysics of variegated leaves

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Analysis of spectroscopic and photophysical properties of plants is relevant to evaluate the physiological state of vegetation and stress factors. In fact, chlorophyll-a fluorescence and reflectance are useful tools to monitor plant health.

The main objective of this work was to study how variegation, alterated pigment composition or the presence of certain reflective features modify the leaves photophysical behaviour, in comparison to conventional green leaves.

For this purpose, homogeneous green leaves (*Ficus benjamina*), purple leaves with high anthocyanin content (*Tradescantia pallida*), variegated leaves with green and yellow sections originated from meristematic tissue unable to generate chloroplasts (*Codiaeum aucubifolium*), and green leaves covered by white trichomes (*Cineraria maritima*) were collected.

Reflectance and transmitance spectra, both in the UV-vis and near-IR, were obtained to calculate absorption (k) and scattering (s) coefficients. Reflectance images were analysed with specialized software in order to obtain photosynthetic pigment content in a non-destructive way. Chlorophyl-a fluorescence emission spectra were recorded and additionally corrected due to light-reabsorption [1]. Quantum efficiency of photosystem II (ΦPSII), photochemical quenching (qP) and non-photochemical quenching (NPQ) coefficients, which are correlated to plants' physiological state and health [2] were estimated from variable chlorophyll fluorescence (known as Kautsky knetics). Finally, leaves images were captured by Scanning Electron Microscopy (SEM) to evaluate foliar surface morphology.

Non-destructive determination of water content in leaves could be achieved succesfully from their absorption coefficients and thickness. On the other hand, the photosynthetic parameters were interpreted in term of the leaves pigmentation.

In conclusion, variegation showed a clear effect upon optical properties (reflectance and diffuse transmitance) and photosynthetic parameters obtained from the fluorescence of intact leaves.

Acknowledgments

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P8-Photobleaching and Regeneration of Camphorquinone in Light-Cured Thiol-Methacrylate Networks.

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The most commonly used visible photoinitiator in resin formulations is camphorquinone (CQ), a blue light sensitive free radical photoinitiator. CQ displays an intense dark yellow color due to the presence of a conjugated diketone chromophore that absorbs at 470 nm. During irradiation of CQ and reduction of one of the carbonyl groups, the conjugation is destroyed, causing a blue shift of the remaining ketone's absorption and loss of the yellow color [1]. This work describes a mechanism to explain the yellowing of initially photobleached thiol-ene networks formulated with Camphorquinone (CQ) as photoactivator. The specimen of pentaerythritol tetra(3-mercaptopropionate) (PETMP)- 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane (BisEMA) resin containing 1 wt% CQ was 10 mm diameter an 3 mm thick.

In a first stage, the CQ is excited under visible light irradiation, to the excited singlet state which converts to the reactive triplet state CQ* via inter-system crossing: free radicals are produced subsequently from two different reactions. CQ* can react with hydrogen donors such as tertiary amines, to generate radicals by electron and proton transfer through a short lived charge-transfer intermediate complex (CTC) to give pinicol and amine derived radicals. Alternatively, in thiol-ene mixtures formulated with CQ in the absence of coinitiator, hydrogen abstraction occurs from the monomer (–S–H), initiating thiol-methacrylate copolymer. CQ itself can photoinitiate methacrylate homopolymerization processes, however, only at a low rate compared to the (CTC) process. Thus, the photodecomposition rate of CQ can be assessed by measuring the decrease in absorbance as a function of the irradiation time by UV–vis spectroscopy (Figure 1, in black).

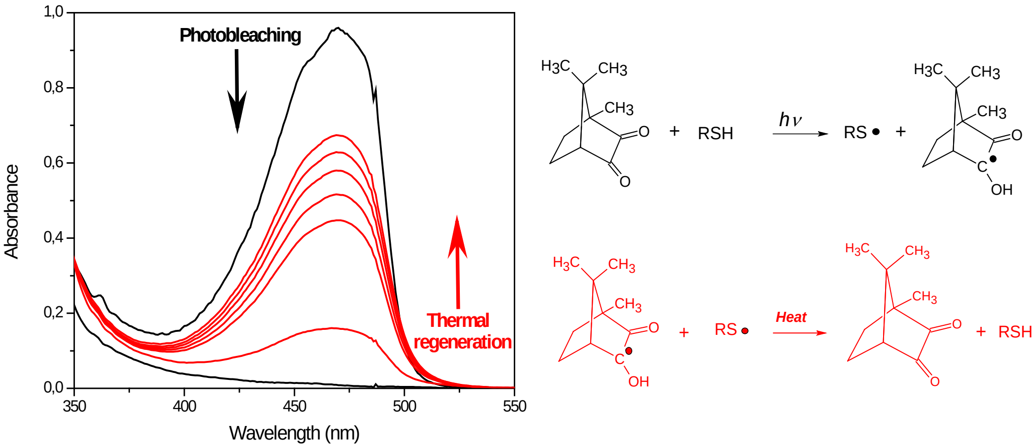

Figure 1. Typical spectral changes showing: photobleaching of CQ by irradiation at 470 nm (black) and the thermal regeneration of CQ (red) and its corresponding equations.

In a second stage, the yellowing in initially photobleached thiol-methacrylate networks was studied by UV visible spectroscopy (Figure 1, red). The yellowing of the networks was apparent after 4 h at 50 ºC, 1.5 h at 70 ºC or 20 min at 110 ºC. However, color changes were perceptible after 40 days at 20 ºC. The change in color observed in the studied polymer networks is explained in terms of the regeneration of CQ through hydrogen transfer reactions between thiyl radicals and ketyl radicals (Figure 1, red equation). Visible light photopolymerization offers many advantages over UV photopolymerization. However, in the particular case of thiol-ene resins photoactivated with CQ, the use of visible light is accompanied by undesired yellowing of the resulting polymers.

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P9-Light Modulates Iron Acquisition in *Acinetobacter baumannii*

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Introduction: In our previous studies we have shown that light exhibits a global effect in the physiology of the human pathogen *Acinetobacter baumannii*. In particular, we have presented evidence that light modulates processes associated with its pathogenicity such as the formation of biofilms, motility and virulence against eukaryotic hosts such as *Candida albicans* [1], and even susceptibility to certain antibiotics [2]. Recently, we identified new traits whose expression are modulated by light in this pathogen such as the PAA catabolic pathway, trehalose biosynthesis, acetoin degradation, and also clusters related to lipid metabolism, bacterial competition such T6SS and tolerance to antibiotics, and determined that these responses depended on the BLUF photoreceptor BlsA [3]. **Objective:** To identify possible BlsA partners and get insights into the mechanism of light signal transduction, we performed pull down experiments. **Methods:** Culture extracts from *A. baumannii* ATCC 17978 cells grown at 24°C in the dark were used to perform pull down assays with His-tagged column immobilized BlsA as bait. **Results:** One of the proteins that emerged as a potential partner of BlsA from pull down experiments is known as Fur, for ferric uptake regulator. Free iron is a limited micronutrient in hosts where it is typically tightly bound within a range of biomolecules, such as heme. As such, iron acquisition systems are important factors for the virulence of pathogenic organisms [4]. Expression of most proteins required for bacterial iron acquisition systems, including siderophore biosynthetic enzymes, are frequently regulated at the transcriptional level by Fur [5]. We therefore decided to evaluate the ability of bacteria to grow in low-iron medium under blue light or in the dark, to determine whether iron acquisition could be modulated by light and study dependance on BlsA. Therefore, growth of *A. baumannii* ATCC 17978 and ATCC 19606 were investigated under varying iron concentrations without shaking under blue light or in the dark at 24°C. Reduction of available iron in LB Difco medium was achieved by supplementation of the media with 2,2'-dipyridyl (DIP), a synthetic iron chelator. In the case of strain ATCC 19606, higher bacterial growth was observed in the dark respect to illuminated conditions. This difference in bacterial growth was lost in the isogenic *blsA* mutants strain, behaving as in light conditions, and the wild type phenotype was rescued by the complementing strain expressing the *blsA* gene from a plasmid. On the contrary, we did not observe significant differences in the growth of strain ATCC 17978 and isogenic *blsA* mutants under such conditions. **Conclusions:** We presented evidence that Fur would interact with BlsA by pull down experiments, and showed that iron acquisition is modulated by light at 24ºC, a process that depends on the presence of BlsA for enhanced growth under iron limiting conditions in the dark. We therefore propose a model that postulates that BlsA binds to Fur in darkness, consequently sequestering the repressor and allowing the proteins required for the bacterial iron acquisition system to be expressed, under iron-limiting conditions. It should be noted that ATCC 17978 harbors additional systems for iron acquisition rather than the only one present in ATCC 19606, the acinetobactin acquisition system, and this could explain the absence of phenotype observed in this strain.

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P10- Photoinactivation of planktonic and biofilm bacterial cultures employing delta-aminolevulinic acid.

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Bacterial Photo-Inactivation (BPI) is an antimicrobial treatment that uses a photosensitizing molecule (FS), which is then irradiated with visible light generating reactive oxygen species and the consequent damage to the microorganisms. On the other hand, antibiotic-resistant infections represent an important clinical problem, most due to the formation of biofilms. Consequently, the need arises for new alternative therapies to the use of antibiotics. In this work we evaluated δ-aminolevulinic acid (ALA) action as a precursor of photosensitive porphyrins [1-2]] in planktonic cultures and biofilms of *Staphylococcus aureus* ATCC 25923 [4], *Staphylococcus epidermidis*, *Escherichia coli* [3] and *Pseudomonas aeruginosa* ATCC 27853. We worked with 24-h biofilms grown over polystyrene plates and planktonic cultures with an OD_{600} 0.7. After incubation in the dark at different doses of ALA, we irradiated the bacteria with a non-coherent white light source. The determination of the effectiveness of the treatments was performed counting colony forming units (CFU/ml). In addition, the amount and type of porphyrins synthesized in the different treatments were determined fluorimetrically and by HPLC. The BPI with concentrations between 1 and 2 mM of ALA, reduces 6 logs the viability of the planktonic and biofilms cultures of the two Gram positive strains analyzed, relative to the untreated controls. In the case of the Gram negative strains, only *P. aeruginosa* showed sensitivity to ALA-BPI in planktonic culture, reducing its viability by 5 logs.

Porphyrins from Gram positive bacteria peaks at concentrations of 1 mM or 2 mM for planktonic or biofilm cultures respectively, concentrations leading to the maximal phototoxicity. In addition, in the case of *S. aureus*, a change in the pattern of porphyrins synthesized can be observed upon increasing ALA concentrations, which is in line with a decrease of the photoinactivation rate.

In conclusion, the results obtained here indicate that BPI employing ALA is an effective treatment, alternative to antibiotics, for Gram positive bacteria in culture and biofilms. In addition, the sensitivity of this treatment is directly related to the pattern and amount of porphyrins synthesized. However, optimization of the BPI treatment in Gram negative bacteria is necessary.

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P11- 3,4-Dihydro-β-carboline alkaloids as potential endogenous photosensitizers

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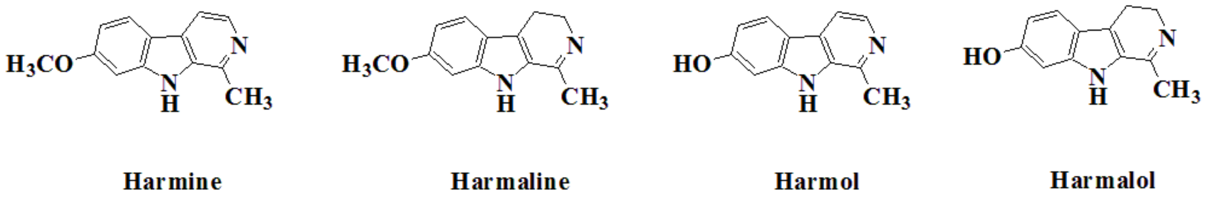
β-carbolines (βCs) represent a family of naturally occurring alkaloids and their presence has been confirmed in a vast range of phylogenetically distant species, *i.e.*, Rhizaria, Alveolata, Amoebozoa, Stramenopiles, Opisthokonta, Archaeplastida, Urochordata and Arthropoda. From the chemical point of view, βCs comprise both full-aromatic and partially hydrogenated (such as 3,4-dihydro- and 1,2,3,4-tetrahydro-) heterocyclic structures. In particular, harmaline and harmalol are the most representative and naturally distributed dihydro-βC derivatives. In terms of its chemical structure, harmine and harmol represent the corresponding full-aromatic structures (Scheme 1).

During the last decade, the photochemistry and photodynamic properties of some full-aromatic βCs have been deeply studied. It has been well documented that these properties strongly depend on the chemical nature of the βC substituent. [1-6] However, the information available in the literature regarding the chemical properties of photo-excited 3,4-dihydro- and 1,2,3,4-tetrahydro-βCs, is still negligible or null and, when available, is somehow contradictory. [7]

In the present work, we have investigated the photochemical behavior of two particular 3,4-dihydro-βCs (harmaline and harmalol) in aqueous solutions under different O_2 concentrations. Also, we examine the capability of these βCs to photoinduce damage in cell-free DNA. Results obtained are compared with data recorded for the corresponding full-aromatic derivatives (i.e., harmine and harmol).



Scheme 1

Acknowledgments: ANPCyT (PICT 2012-0423 y 2013-2536).

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P12- Direct and photosensitized attenuation of *Toxoplasma gondii* tachyzoites

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Toxoplasma gondii is a protozoan obligate intracellular parasite that can infect a wide range of animals including approximately one-third of the human population. Infection can result in severe clinical diseases.[1] In addition, infection in domestic animals is a threat to public health from food-borne outbreaks and causes a great economic loss as it may lead to abortion, stillbirth and neonatal loss.[2] Therefore, toxoplasmosis is of great medical and veterinary importance. Treatment of this disease is difficult since the available drugs have severe side effects and reactivation may occur at any time.[3] Under the present scenario, therefore, developing an effective vaccine against *T. gondii* infection is the need of the hour.

The vaccines based on live-attenuated parasites are more efficient than vaccines based on dead-parasites, because the former ones emulates the natural infection. [4] In this regard, γ, X-ray and UVC radiation have been used as attenuation sources of a remarkably wide range of parasite species [5,6]. In every case, irradiated parasites induce protective immunity against subsequent challenge of experimental hosts.

Regarding UVC irradiation, parasite's attenuation may occur either due to direct absorption of the incident radiation by molecular targets or mediated by reactive oxygen species leading to a highly oxidant environment. Such an environment can certainly induce unspecific and uncontrollable damage on both morphological and functional aspects of the parasites. Thus, the type and/or extent of damage and, consequently, the immunogenicity, would depend on the UVC doses applied.[7] Therefore, other attenuation sources such as UVA and visible radiation, *via* photosensitization, should be taken into account and further evaluated.

In the present work, a systematic and comparative evaluation of the effect of three different types of radiation (UVC, UVA and visible) as attenuation sources of *T. gondii* tachyzoites has been carried out. In particular, we have evaluated the effect on morphological (structure and proteins stability, etc.), intracellular Reactive Oxygen Species (ROS) production and physiological functions (invasion and replication capability) of *T. gondii* tachyzoites.

ACKNOWLEDGEMENTS

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P13- Comprehensive chemometric analysis of β-carbolines alkaloids

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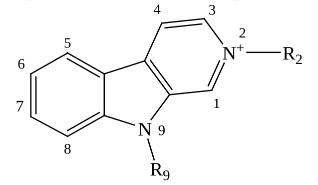
Derivated of β-carboline (βC) alkaloids has were found in a wide range of species [1-4]. In mammals, they have an exogenous (diet) [1] and endogenous origin (biosynthesis) [2]. In particular, N-methyl-βCs has been reported as potential pathogenetic factors in Parkinson's disease, inhibitors of acetylcholinesterase enzyme, neuroprotective and neuron-differentiating agents, antimicrobial compounds, and DNA intercalators *in vitro* [3a-e]. So despite the established importance of N-methyl-βCs and related βCs, the molecular bases of the mechanisms involved on the above mentioned processes still need to be addressed. In this regard, a deep knowledge of fundamental aspects related to their spectroscopic, chemical and photophysical properties represents a key starting point. It is known that for βCs the latter properties strongly depend on the chemical molecule structure, as well as on the nature of the environment (solvent) and its pH [4]. In consequence, each specific βC derivative deserves special attention, particularly for better assessing the correlation between alkaloid acid-base species and their physico-chemical properties. Hence, we have systematically investigated photophysical properties of *nor*harmane (nHo) and their N-methylated derivatives (Scheme 1), in aqueous solution, paying special attention not only on the equilibrium and/or species dominant in physiologically relevant pH-conditions but also under highly alkaline conditions. As in many cases the species involved have a high degree of spectral overlap and the extraction of information is not possible with traditional analysis tools (univariate data), the use chemometric methods (multivariate analysis techniques) was exploited for interpretation and analysis of the spectroscopyc data, providing qualitative and quantitative information about equilibria and species involved.

βCs are naturally occurring secondary metabolites that deserve to be explored in several fields of biology because they might represent an interesting alternative as fluorescent tracers endowed with unique photophysical properties. The results of the present work would contribute to understand the photophysical behavior of βCs in biological environments and, therefore, to further elucidate the roles played by these alkaloids in a wide range of biological systems. In addition, this study also shows that multivariate analysis provides a reliable tool for tracking bioactive compounds in natural product extracts.



Scheme 1: Chemical structures of β-carbolines studied in the present work

Short name, salt name, (abbreviation)	R_2	R_9
*Nor*harmane, (nHo)	-H	-H
*Nor*melinonine F or 2-Methyl-*nor*harmanium, 2-Methyl-*nor*harmanium iodide, (2-Me-nHo)	$-CH_3$	-H
9-Methyl-*nor*harmane, (9-Me-nHo)	-H	$-CH_3$
2,9-diMethyl-*nor*harmanium, 2,9-diMethyl-*nor*harmanium iodide, (2,9-diMe-nHo)	$-CH_3$	$-CH_3$

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P14- The effect of PDT based on ALA and its derivatives in 3D ovary cancer models

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Over the last decade, the employment of 3D models in cancer assays has grown. Spheroids have been shown to be much less sensitive than monolayer cells in treatment response studies, where physical variables such as penetration reflect a more realistic scenario [1]. On the other hand, it has been determined that 3D oncospheres are enriched in stem-like cells, which are often related to the development of metastasis and persistence after chemotherapy [2]. Thereby, 3D models allow us to study keys of photodynamic therapy (PDT) efficiency and its importance as a synergic treatment.

PDT is a treatment for tumors of easy access by endoscopic route, like the ovarian cancer, based on the preferential accumulation of the photosensitizers in the malignant tissue after administration and the subsequent exposure to light [3]. This combination promotes reactions mediated by reactive oxygen species, which destroy the tumor cells. Since ovary cancer in most cases presents peritoneal dissemination at the time of diagnosis [4], the use of 3D models mimicking peritoneal metastasis, constitutes an interesting approach.

Our group is specialized in PDT with the photosensitizer Protoporphyrin IX biosynthesized from its precursor, 5-aminolevulinic acid (ALA) and its derivatives synthesized to increase its penetration [5]. Among the latter, we used the 89-ALA and 95-ALA conjugates, as they synthesized more porphyrins at lower concentrations than those generated by ALA and thus giving better effectiveness.

In the present work, we tested the response to PDT based on ALA and its derivatives in 3D spheroids as compared with monolayer cultures of IGROV-1 and SKOV-3 ovary cancer. We also analyzed the PDT response of oncospheres of the same cell lines enriched in stem cells.

Analysis of viability through the MTT assay was performed. In addition, use of imaging metrics (area, circularity, sphericity and density) allowed us to evaluate certain effects that cannot be achieved through traditional methods.

Spheroids showed a decrease in cell survival after PDT with all the photosensitizer, being 95-ALA the most efficient. However, a degree of resistance to the treatment was observed as compared to monolayer cultures of the same line, and this may be due to a lower degree of penetration of either light or photosensitizer to the inner layers of the spheroids. In addition, the analysis of images prior and after treatment indicated an increase of diameter, associated with a clear disruption of the micronodular structure. Finally, oncospheres enriched in stem cells exhibited a greater resistance to PDT than monolayers.

In conclusion, the observations detailed herein highlight the potential value of the use of PDT in the treatment of ovary cancer dissemination, in combination with antineoplastics. In addition, the use of ALA derivatives improves ALA performance, thus reinforcing the importance of photosensitizer penetration in 3D models.

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P15- Photochemical behaviour of Fisetin and Fisetin-Copper(II)

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Introduction: Fisetin (Fis) is a polyphenolic compound with interesting antiviral, antioxidant, and other biological properties [1]. Fis also have the capacity to complex a wide variety of metallic ions which could affect their bioactivity. In the present work, a photochemical study of Fis and its metallic complex (Fis-Cu(II)) was carried out.

Results and discusions: The Riboflavin (Rf)-sensitized photoirradiation of Fis and Fis-Cu(II) at H2O/EtOH 70:30 v/v medium produced spectral changes that can be attributed to transformations in both substrates. The oxygen uptake in presence and absence of specific quencher of reactive oxygen species (ROS) made evident the interaction between Fis and H2O2, showed by the decrease of the O2 consumption rate in presence of catalase, whereas in the case of Fis-Cu(II) complex the experimental results allow to confirm the participation of the O2•- species in the oxidative process, but no significant evidence of singlet molecular oxygen (O2(1Δg)) interaction was observed. Nevertheless, on the basis of our previous investigations where this ROS usually plays a rol in the photooxidative mechanism of flavonoids, the rate constant for the overall interaction with O2(1Δg), kt, was determined through a Stern-Volmer treatment (see values in the table). The phosphorescence quenching experiments demonstrated the existence of a O2(1Δg)-Fis and Fis-Cu(II) interaction. The reactive O2(1Δg) quenching constants (kr) were determinated for both systems and are showed in the table.

System	k_t x 10^{-7} $M^{-1}s^{-1}$	k_r x 10^{-7} $M^{-1}s^{-1}$	k_r/k_t
Fis	14.4	0.26	0.02
Fis-Cu(II)	7.25	2.66	0.36

The kr/kt ratio is an useful parameter of the substrate oxidability since indicates the fraction of overall quenching of O2(1Δg) that effectively leads to a chemical transformation. It can be seen that the interaction of Fis-O2(1Δg) is exclusively physical. On the other hand, the metallic complexation of the flavonol increases the reactive fraction, reaching 36 % of the overall interaction. The anaerobic photodegradation of Rf under visible light irradiation predominantly proceeds through the triplet state [2], and the rate of the process can be estimated by absorption spectroscopy. Comparative irradiations of N2-saturated ethanolic solutions of Rf under identical experimental conditions, in the absence and in the presence of either Fis or its metallic complex were carried out. Hence, data were evaluated through a simple Stern-Volmer treatment being the apparent rate constant values for the process of quenching of 3Rf∗ close to 1,4x1010 M-1s-1. This step could contribute to decrease the stationary concentration of O2(1Δg) and, therefore, to present a protective effect against this species.

Conclusions: Fis and its complex are physical deactivators of O2(1Δg), increasing the reactive component for the latter one. The oxygen uptake in presence and absence of specific quencher of ROS made evident the participation of H2O2 in photooxidation of Fis, meanwhile O2●- is the main ROS in its metallic complex photoconsumtion.

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P16- Oregan Essential Oil: interaction with photogenerated singlet molecular oxygen

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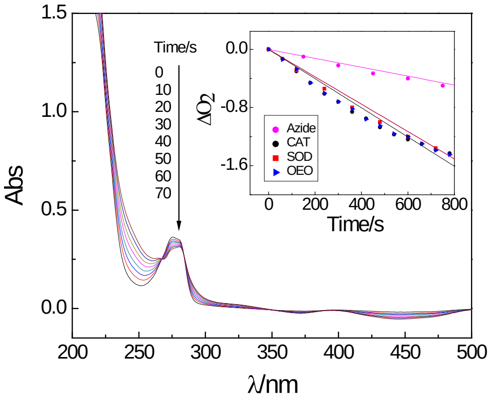
Introduction: Essential oils are a mixture of volatile compounds, products of the secondary metabolism of plants. Once these oils are extracted, they can be deteriorated losing their organolpetic and therapeutic properties due to various environmental factors. Exposure to light in aerobic conditions is the main cause of these decomposition and leads to the generation of allergenic compounds responsible for dermatitis, eczemas, among others [1]. These degradations can be caused by reactive oxygen species (ROS) photogenerated from endogenous sensitizers. In this work the photodegradation of the essential oil of oregano (OEO) in presence of vitamin B2 (Riboflavin, Rf) was studied.



Experimental: OEO was extracted by hydrodistillation with Clevenger trap from plants grown in the experimental field of the FTU-UNSL, which were in flowering state. The main compounds of OEO, carvacrol (CR) and thymol (TM), were characterized by EIMS and NIST Mass Spectrometry Data Center. In addition, CR and TM were quantified, in the extracted oil, by gas chromatography (see Table 1). The mixture Rf + OEO was irradiated at $\lambda >$ 400 nm in solvent MeOH: H_2O 60:40 v/v and the spectral evolution is shown in the figure, indicating OEO reacts with photogenerated ROS. In order to identify the participating ROS in the photodegradation mechanism of the OEO, experiments of oxygen consumption of solutions in the presence and absence of specific ROS inhibitors were carried out [2]. Oxygen consumption profiles indicate degradation occurs involving singlet molecular oxygen ($O_2(^1\Delta_g)$) (see inset). The total quenching rate constant of $O_2(^1\Delta_g)$, k_t, and the reactive quenching constant, k_r, of OEO and its two major components were determined (see table). The k_r/k_t ratio was calculated since it indicates the fraction of overall quenching of $O_2(^1\Delta_g)$ that effectively leads to a chemical transformation.

Table 1. Kinectic constants of OEO, CR and TM

System	k_t x 10^{-6} $M^{-1}s^{-1}$	k_r x 10^{-6} $M^{-1}s^{-1}$	k_r/k_t
TM	5.6	1.7	0.3
CR	4.7	1.1	0.2
OEO	4.6	2.4	0.5

Discusion: Degradation of OEO, CR and TM in the presence of Rf involves participation of $O_2(^1\Delta_g)$, mainly through a physical process. The observed values of k_r/k_t suggest that with OEO, the chemical reactivity component is higher compared to CR and TM. This indicates that other species could contribute to reactive photoprotection from OEO.

Acknowledgments: Financial support from CONICET and SCyT of the Universidad Nacional de San Luis and Universidad Nacional de Río Cuarto, all from Argentine, are grateful acknowledged.

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P17- Influence of the alkyl chain length on the coumarins chalcones location on liposomes: DPPC, POPC and mixtures of DPPC/POCP.

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The use of fluorescence probes for monitoring biological membrane properties has permitted to determine microscopic properties such as fluidity and permeability, and also more complex phenomena like microdomain formation in mixtures of lipids. In the recent years, we have been interested in the use of 7-amino coumarin, a choromophore that presents a large bathochromic shift on the absorbance and fluorescence with polarity of the media. This behavior has been interpreted in terms of a locally excited state (LE) in non-polar solvents and internal charge transfer excited state (ICT) from the amine group to lactone carboxylic group the in polar solvents. [1,2]

In the present work, we have synthesized 7-aminocoumarin-chalcone with different hydrocarbon chain length ($C_{334\text{-CHx}}$, Figure 1A) for modulating ICT formation in coumarin probes in liposome. Interestingly, this probe showed larger bathochromic and stock shifts in polar solvents suggesting formation of ICT species. Experimental and Theoretical calculus results allow us to explain that behaviour photophysic of $C_{334\text{-CHx}}$ must be the formation of a twisted intramolecular charge transfer (TICT) (not shown) competing with a LE state and ICT excited state. In addition, we have evaluated the dependence of the TICT excited state with the membrane fluids at different temperatures in liposomes (Figure 1). Finally, we have determined the most favorable position of coumarins chalcones with different hydrocarbon chain in membrane models by molecular dynamics.

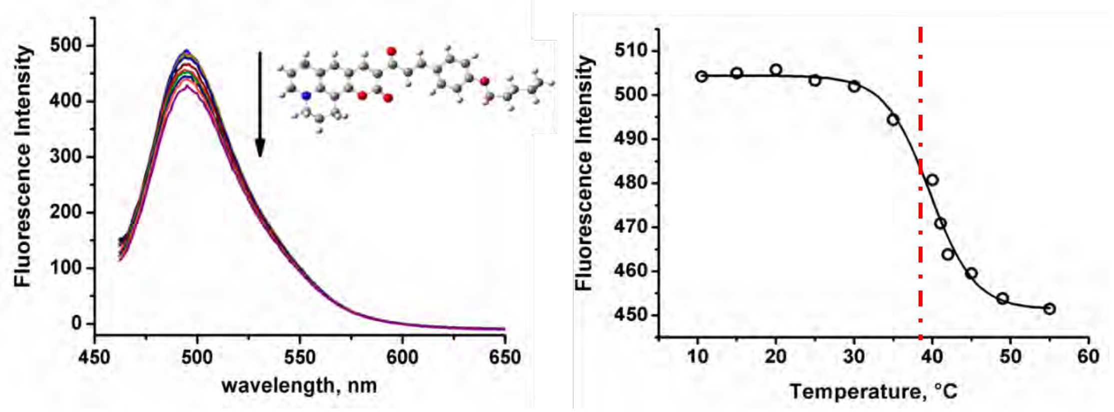

Figure 1. (A) Fluorescence intensity of C334-CH-10 in liposome of DPPC, (B) and Changes in the emission of fluorescence at different temperatures of C334-CH-10.

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P18- Optimization of Second Generation Photosensitizers by Vehiculization in Polyacrylamide Nanoparticles.

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Polyacrylamide nanoparticles (PAA-NPs) are promising vehicles for the incorporation of drugs in photodynamic therapy (PDT) and photodynamic inactivation (PDI). The polymeric matrix of PAA-NPs protects the active form of the photosensitizer (PS) from possible enzymatic degradations or from the biological environment and prevents its aggregation. Thus, new NPs of different PAA, (2-hydroxyethyl methacrylate (HEMA-NPs) and (+) N,N´-Diallyl-L-Tartardianide (DAT-NPs), were synthesized to incorporated two second generation PS: monobrominated Neutral Red (NRBr) and monobrominated Azure B (AzBBr), with activity in PDT and PDI [1-2]. In this study, the PAA-NPs were prepared based on the inverse microemulsion polymerization. The obtained HEMA-NPs and DAT-NPs were characterized by size and zeta potential analysis with promising results. In addition, the oxidative activity was evaluated. Photooxidation of 9,10- Anthracenediyl-bis (methylene) dimalonic acid (ABDA) was also used to determine oxygen quantum yield (Φ_Δ) by the photosensitizers. NRBr and AzBBr were used as references (Φ_Δ= 1).
According to the obtained results, it is possible to affirm that for the NRBr dye, the production of singlet oxygen increases considerably when this one is loaded in the nanoparticles, in comparison with it is free in water. Thus, for NRBr-HEMA-NPs, the value of Φ_Δ was 3.5 times greater than that obtained for free NRBr. While NRBr-DAT-NPs, the value of Φ_Δ tripled to the free PS. These results are very promising and would indicate that the PAA-NPs have the capacity to induce the reactive oxygen species generation of PS and lead to the formation of more singlet oxygen at the site.
On the other hand, for the AzBBr, the observed behavior was similar to that for NRBr, the thiazine vehiculized dye, caused greater decomposition of ABDA than the free one. From the above, it can be deduced that the vehiculization of these dyes (NRBr and AzBBr) in the PAA-NPs is able to optimize the photochemical properties of the PS, which is an important advantage for the probable applications of these.

Acknowledgments

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P19- Green fluorescence pyrene-based dye: study of photophysical and photochemical properties

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Pyrene is a polycyclic aromatic hydrocarbon (PAH) characterized by a blue emission with long lifetime decay (τ) and high fluorescence quantum yield (Φ_f) [1]. The electronic, photophysical and fluorescence properties of pyrene and its derivatives are very attractive which have resulted in a variety of applications including transitors, OLEDs, supramolecular photosensors and photosensitizers in photodynamic therapy. The main reason for the extensive application of pyrene in diverse scientific fields is the facile control over the structural and electronic properties by chemical manipulation [2]. We developed a new π-extented system from pyrene by coupling phenylethynyl groups on the 4-(pyren-1-yl)butanoic acid core structure by Sonogashira method. The result compound, 4-(3,6,8-tris(phenylethynyl)pyren-1-yl)butanoic acid (TPPy), shows a bathochromic shift for both absorption and emission Spectra relative to pyrene (Figure 1) and a highly efficient green light emition. The main photophysical/photochemical parameters obtained can be observed in Table 1.

A small bathochromic shift (*c.a.* 6 nm) of the UV-vis spectra is observed when the solvent is changed from CCl_4 to DMSO, which can be attributed to π-π* transitions. Further, the molar extinction coefficients (ε) are large (10^4 $M^{-1}cm^{-1}$) and substantiate the π-π* nature of the electronic transitions. The singlet oxygen quantum yield (Φ_Δ) was measured by direct detection of the 1270 nm emission (singlet oxygen emission), from which the value Φ_Δ=0.40 (CCl_4). The effect of concentration was investigated in THF and more concentrated solutions of TPPy (10^{-2} mol L^{-1}) reveals both a change in the relative intensity and a small red shift of the bands. A broad shoulder is readily observed above 530 nm, attributed to the excimer formation. The time resolved emission decay spectra were obtained at 1, 3 and 19.5 ns after the laser pulse and the band ratio changes as time evolves, similar to the concentration effect. The formation of the excimer in solution occurs 1.88 ns after the laser pulse with a spectral pattern different from the solid state emission. Further, by following the emission at 530 nm it was found that the rate constant for excimer formation was 5.32×10^8 s^{-1}.

The structure of TPPy was investigated by density functional theory (DFT) calculations. The results corroborate the participation of the phenylethynyl groups as part of the structure of both the HOMO and the LUMO orbitals, thus explaining the red shifted emission, relative to pyrene as a consequence of the extended π-conjugation.

Tab.1. Photophysical/photochemical properties of TPPy (10^{-6} mol I

Solvent (25 ºC)	λ_{abs} (nm)	log ε (M^{-1} cm^{-1})^a	λ_{em} (nm)	Stokes shift (nm)	Φ_f
CCl_4	260, 330, 420, 445^a	4.76	460^b, 490, 525	15	0.56
DMSO	260, 335, 430, 451^a	4.81	461^b, 490, 520	10	0.72

a-Absorption maximum **b**-Emission maximum

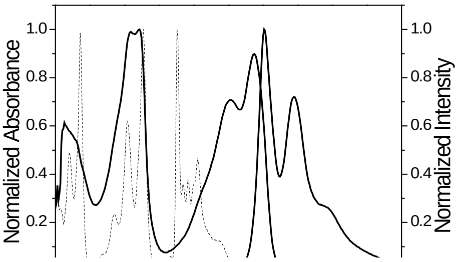

Fig.1. UV-vis absorption and emission spectra of TPPy at 10^{-6} mol L^{-1} in DMSO (line) and comparison with pyrene (dashed).

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P20-Flavonols photoacidity: rationalizing excited state intramolecular proton transfer reactivity

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Photoacids are molecules that become strong acids at the excited electronic state[1]. Typically, these compounds are aromatic alcohols, and are useful to study kinetics mechanisms of proton transfer reactions or as a way to create sudden variations of pH (pHjump)[2]. In this context, it can be found the flavonols, which are natural phenolic compounds that present antitumoral, antiinflamatory and, specially, antioxidant characteristcs[3].The antioxidant properties of flavonols play an important role on plant protection, which are directly linked to phenolic acidity of the flavonol hydroxyl moiety[4]. In this sense, these features encourage us to evaluate experimentaly the acidity constants on the ground and excited states (pKa and pKa*) of a series of flavonols, as 3-hydroxyflavone (3HF), 4’-diethylamino-3-hydroxyflavone (DEA3HF) and 4’-fluoro-3-hydroxyflavone (F3HF) (Figure 1). The constants were obtained from spectrometric titration using the UV-Vis absorption spectra in a mixture of water and ethanol (1:1) to pKa, and fluorescence emission spectra in water to pKa*. Furthermore, to explain the origins of the photoacidity on this series, theoretical calculations under the density functional theory (DFT) framework using the functional CAM-B3LYP/6-311++G(d,p) were also performed.

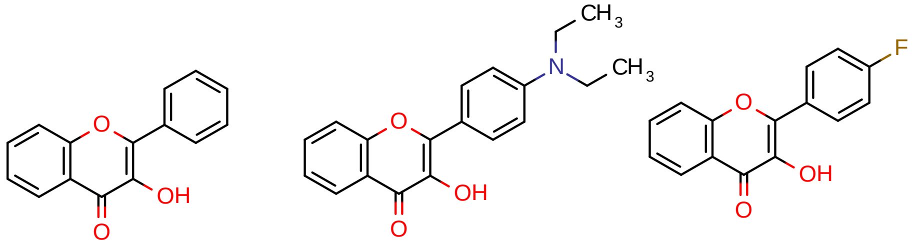

Figure 1: Molecular structures of 3HF, DEA3HF and F3HF, respectively.

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P21- Effect of adding photoprotective compounds in the diet of *Palaemon macrodactylus* and its role under ultraviolet radiation

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Palaemon macrodactylus is a successful invader, known as the Oriental Shrimp, native to estuaries and coastal waters of the Northwest Pacific. In the south western Atlantic, the species was found in Mar del Plata harbour, Argentina, probably introduced from the Pacific with discharged ballast water [1]. During the past two decades, it has shown an increase in ultraviolet radiation (UVR) and particularly the UVB (280-315nm) above Earth's surface. There is some evidence that UV-B radiation (280-315 nm) and the shorter wavelengths of UV-A (315-400 nm) can significantly affect the biota in waters up to 20 m deep [2] and have adverse physiological effects on aquatic organisms such as damage in the genetic material and high mortality. It has been shown that many species of seaweeds synthesize and accumulate high concentrations of photoprotective compounds and may constitute an interesting alternative as a supplement in aquaculture feeds. The aim of this study was to determine the bioaccumulation of photoprotective compounds (PPC) from diets added with red seaweeds meal of the family Halymeneaceae on juvenile *P. macrodactylus* and its possible protective role under conditions of stress by UVR.

Juveniles of *P. macrodactylus* collected from Mar del Plata harbour (38° 03′ S; 57° 31′ W) were placed in PVC tanks under controlled conditions of temperature, pH, and salinity, under two feeding treatments: one group with basal diet (B) (45% protein, 8% lipid, 7% water and 7% ash) and the other 2% diet added with red seaweed meal of the family Halymeneaceae (diet B2). After 15 days animals were subjected to two radiations in four treatments, by triplicate: a) Control PAR (400-700nm) and diet B b) PAR+ UVR (280-700nm) and diet B c) PAR and diet B2, d) PAR+ UVR and diet B2. Survival, percentage of weight gain, concentrations of PPC and carotenoids were determined.

In treatment b mortality of 16% was recorded after 72 hours of exposition to UVR, while in those fed with the 2% added diet, the same mortality was observed after 120 h of exposure. Survival in the treatments (a, c) was 100%. At the end of the exposure radiation period, percentage of weight gain was higher in animals fed with diet B (77%) nevertheless concentration of PPC and carotenoids (determined as OD g tissue^{-1}) recorded the highest values in the animals corresponding to treatment c (PPC: 1.9 ± 0.38 DO g^{-1}; carotenoids: 0.48 ± 0.1 OD g$^{-1)}$. although there were no significant differences between other treatments.

These results suggest that, a diet added with red seaweeds rich in photoprotective compounds constitutes and interesting alternative, not only for its contribution to a better physiological state of animals under stress conditions by UVR, but also for the particularity of being invasive species with potential commercial use.

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P22- Silver Nanoplates for Thermal Therapy of Cancer

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Utilization of thermal therapy (hyperthermia) is defined as the application of exogenous heat induction for treating various diseases. In general, hyperthermia is applied as adjuvant means in therapeutic protocols combining chemotherapy and/or irradiation both of which can induce irreversible cellular DNA damage [1].

New prospects for light-activated therapies have been emerged in recent years by exploiting the unique optical properties of noble-metal nanoparticles. When the incoming light couples with the oscillation frequency of the conduction electrons in noble-metal nanoparticles, a so called localized surface plasmon resonance (LSPR) arises, which is manifested as a strong absorption band along with an efficient photo-to-heat conversion (photothermal effect) [2]. More specifically, when localized in the tumor, the plasmonic nanoparticles can act as efficient photothermal transducers by converting the light absorbed by surface plasmon resonances into heat, leading to a localized rise of temperature, thereby achieving therapeutic cell killing [3,4].

We have synthesized silver nanoplates with PEG (polyethylene glycol) and PVP (polyvinylpolypyrrolidone) cappings. TEM images allow us to see the shape and size of the particles. UV-visible absorption spectra showed that the LSPR maxima of the three nanoparticles are located between 700 and 800 nm. These wavelengths are within the near-infrared (NIR) window, where light has its maximum depth of penetration in tissue. ATR-FTIR spectra of the nanoplates were measured to confirm the effective coating.

Suspensions of different concentration of each nanoparticle 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 nanoplates. The temperature increase for the suspensions of the nanoparticles is larger than those observed upon irradiation of water and a calorimetric reference, used as controls. These in vitro assays seem to indicate that the nanoplates are good candidates to be employed in photo-thermal therapy.

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P23- Interaction of Core-Shell SiO_2@Ag Nanoparticles with Excited States of Sensitizers

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Because of our interest in the influence of nanomaterials on the photodynamic therapy of tumors (PDT), we here studied the effect of core-shell SiO_2@Ag nanoparticles on the aqueous photophysics of three sensitizers: the anionic Rose Bengal (RB), the neutral Riboflavin (Rf), and the cationic Methylene blue (MB). All these sensitizers were shown to present photodynamic action: RB on gram positive and gram negative bacteria [1], Rf on corneal scrapings of patients diagnosed with a fungal keratitis [2], and MB on different human breast cell lines [3].

The core-shell SiO_2@Ag nanoparticles were synthesized by a combination of modified reported methods. Briefly, the electrochemical deposition of silver nuclei on the surface of Sn^{2+}-modified silica spheres [4] was followed by photochemical growth of the nuclei employing the photo-reducing agent I-2959, which upon irradiation generates a ketyl radical able to reduce Ag^+ to metallic Ag [5]. The nanomaterials were characterized by TEM, DLS, zeta potential measurements, and UV-visible spectroscopy.

UV-visible spectroscopy, steady-state and time-resolved fluorescence spectroscopy, and ns-transient absorption spectroscopy data indicate that the interaction between the dyes and the negatively charged SiO_2@Ag nanoparticles is strongly dependent on the sensitizer.

No interaction between SiO_2@Ag and the anionic RB was observed, whereas evidence for the adsorption of the cationic MB on the nanoparticles was obtained. As a result of the adsorption, the decay of the triplet state of MB in suspensions of SiO_2@Ag showed a biexponential decay with contributions of the free and sorbed dye.

For the neutral sensitizer Rf, there is metal-enhanced fluorescence, and no evidence for the absorption of the triplet state of the dye is found with ns excitation. Besides, formation of a long-lived neutral radical (protonated form of $Rf^{\cdot -}$) is observed. However, data obtained with Rf in suspensions of the SiO_2 nanoparticles without the Ag shell show a triplet decay in the μs range, as also observed in the absence of the particles. These results are interpreted in terms of a reaction mechanism, which includes the electron transfer on the surface of SiO_2@Ag from metallic silver to the singlet excited state of Rf.

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P24-Photopolymerization reactions initiate dusing visible light

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Photopolymerization reactions requires absorption of ultraviolet or visible radiation in in order to initiatethe process[2]. The photoinitiatoris a molecule that, by absorbing light at a given wavelength, generates excited states that by cleavage of a chemical bond, electron transfer or hydrogen abstraction, leading to the formation of extremely reactive species[3]. Systems containing substituted pyrene rings are receiving prominence for appear as prominent photoinitiators, due to improving the solubility of these compounds in the main commercial monomers[1]. This work aimed to synthesize a new ketone photoinitiator derived from pyrene, 2,2-diphenyl-1-(pyren-1-yl)ethan-1-one (DiPhPy), capable of initiating photopolymerization reactions using butyl acrylate as monomer and employing light in the visible region.

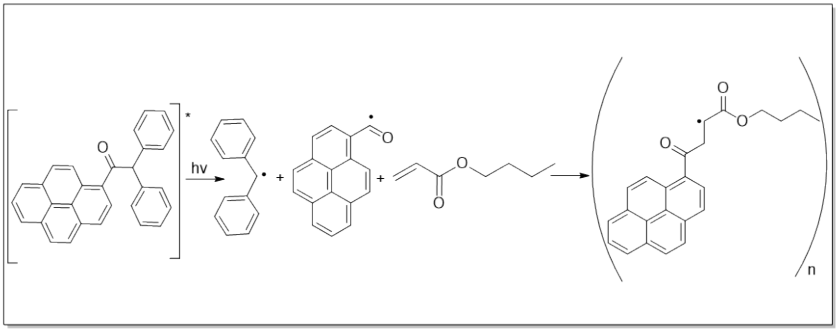

Fig. 1 - Schematic of the photopolymerization reaction using DiPhPy

The results showed that the photoinitiator synthesized was able to initiate the photopolymerization reaction, giving rise to a fluorescent polymer. The characterization of the triplet state was done using bixin, with the maximum absorption of this transient at 450 nm and life time of 15.3 μs in acetonitrile. It was possible to observe the formation of the radical pyrene cation, at 460 nm, using methylviologene as quencher.

Acknowlegments:CAPES and Chemistry Institute UFRJ.

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P25- Hydrophobic effect on the quenching mechanism of small coumarin-peptides derivatives by Trp

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Photophysical and photochemical properties of coumarin 314 (C_{314}) have been employed for synthesizing different fluorescent molecular probes responding largely to the polarity of the solvent.[1] In addition, laser flash photolysis studies showed the formation of triplet excited state in benzene (λ_{abs}= 550 nm) and free radical species in aqueous solution (λ_{abs} = 370 nm) formed by electron ejection from an internal charge transfer excited state (ICT).[2]

In this work, we studied the photophysics of C_{314} derivatives (C) with free tryptophan (Trp) and Trp-containing peptides, where C is linked to a Tyr residue in synthesized peptides:

C-Tyr-Trp-Arg-Arg (1), C-Tyr-Pro-Trp-Arg-Arg (2), C-Tyr-Aib-Trp-Arg-Arg (3)

Owing to the observed dynamic and static quenching elicited by free Trp on the C_{314} fluorescence different spacer residues between Tyr and Trp were included, modifying the rigidity/flexibility of the backbone that has permitted to modulate the intramolecular quenching. In particular, fluorescence lifetimes and relative quantum yield measurements showed a major quenching for the peptide (3), which holds an Aib spacer residue. However, spectral absorption and fluorescence changes, lifetimes, and chromatography studies of HPLC-DAD/FL and UHPLC-MS/MS suggest an intermolecular equilibrium associated with dimer formation and intramolecular adducts derived to the interaction between Trp residue and coumarin moiety. To evaluate the nature of the Trp-C interaction, we realized quenching measurements in the presence of urea, a chaotropic agent that can disrupt the hydrogen bonding network. The results of the quenching elicited by free Trp and Trp-containing peptides on the C314 fluorescence presented a dynamic quenching with a considerable decrease on the static quenching mechanism, which is promoted by water hydrophobic effect (Fig. 1).

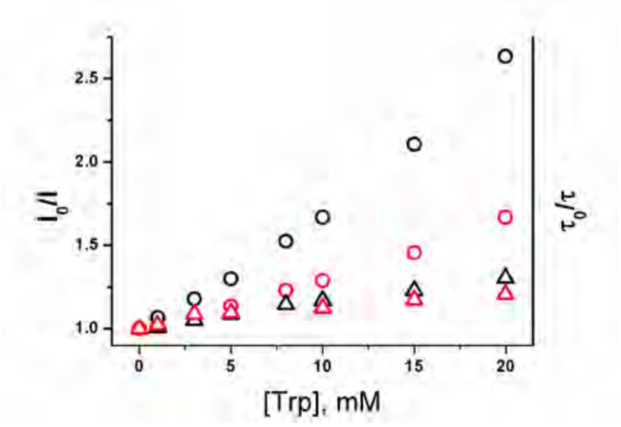

Figure 1. Stern-Volmer plots of C_{314} quenching elicited by free Trp using fluorescence intensities (○) and lifetimes (Δ) in presence (red) and absence (black) of urea, in 20mM buffer pH 7.

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P26- Effect of the presence of oxygen on the photochemical dehalogenation of dehydropyridines and isophthalonitrile derivatives.

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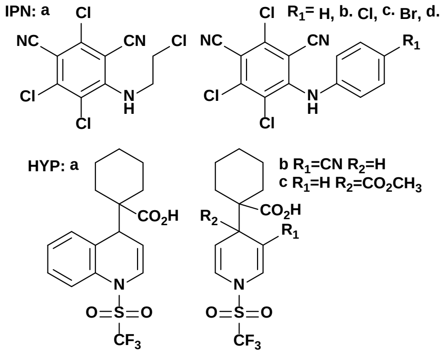
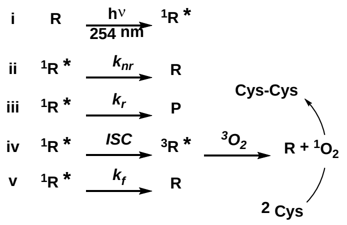


Figure 1. Isophthalonitrile (IPN) and dihydropyridine (HYP) derivatives under study.



Scheme 1. Possible reaction paths of the excited state analyzed.

As part of our ongoing project on the reactivity of halogenated compounds, we are exploring halogenated systems such as isophthalonitrile (IPN) and hydropyridine (HYP) derivatives, figure 1. We are interested in these compounds since pyridines emerge as one of the most prevalent structural units in pharmaceutical and agrochemical targets, as well as in material science [1], while chlorinated isophthalonitrile derivatives have a potencial usage as fungicides[2]. Our study aims to analize and comprehend the reactivity after irradiation ($\lambda = 254$nm), the identity of the photoproducts generated under different enviroments (presence or absence of O_2) and the knowledge of all possible reaction paths of the excited state, scheme 1 i-v.

We present the analysis of the disappearance rate constants for the compounds of figure 1, under different conditions. All photolysis reactions had a linear decay with time, so it can be concluded that the process is of first order. For IPN derivatives, even though at the wavelength of photolysis the samples have a considerable molar absorptivity coefficient (ε), the k_r at which some of them are being photolized are rather small and they resulted to be higher in the absence of oxygen in the medium. For HYP derivatives in contrast, no significant differences were observed in terms of the presence of oxygen but the k_r were significantly higher. These facts indicate that the excited state is taking different paths for IPNs and HYPs. The presence of O_2 plays a significant role in the photodegradation mechanism of IPNs. A possible role could be the formation of $^1O_2$ via an energy transfer process which has been probed with an indirect approach. It is well known that L-cysteine in the presence of $^1O_2$ forms L-cystine through a soft oxidation. Therefore, a solution of reagents/L-cysteine was irradiated in the presence of O_2 and the formation of a white solid identified as cystine was observed confirming the occurrence of 1iv with high quantum yield. Other possible path that was tested, is fluorescence. Therefore, we measured the fluorescence spectra but the quantum yields determined were of the order of 10^{-3} in all cases. Measurements were done relative to $Ru(bpy)_3^{2+}$ as standard [3].

Therefore, for HYPs decomposition is the path with the highest quantum yield as singlet oxygen formation is the prevailing path for IPNs. In relation to the photoproducts formed, for IPN derivatives dechlorination and decyanation took place with small quantum yields, while for HYPs the loss of the -SO_2-CF_3 moiety as well as re-aromatization processes occurred with high quantum yields.

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P27- Searching for real antioxidants for food industry; anti and pro oxidantactivity of jaceidinfrom *Zinnia peruviana*.

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The consumption of antioxidantsupplementsin well-nourished populations have been increasing because theyareassociated to the prevention of cardiovascular diseases, cancer and aging processes [1]. Packaged Facts (Consultant of market information for top industry decision makers) estimates that antioxidant featuring foods, beverages, supplements, and personal care/cosmetics totaled $65 billion in U.S. retail sales in 2014 and up 9% over 2016. By 2018, the market is projected to approach $86 billion [2]. In past decades, several researches have documented the efficient activity of antioxidants,althoughrecent studies suggest that antioxidants in addition to scavenging free radicals, may have the opposite effect and promote or even accelerate the development of tumors [3,4].

Singlet oxygen ($^1O_2$) can be generated by photochemical reactions type II, and its detection is possible by either spectroscopic technics [5].However, due the increasingly contradictory reports about the pro-oxidant effects of these and other antioxidants, the aim of this research was to evaluate the ability of the flavonoid"jaceidin"obtained from *Zinnia peruviana*to photosensitize the generation of $^1O_2$using the photo-oxidation of L-tryptophan (Trp)as an indirect detection method.Steady state photolysis of Trpwas studied following the decrease of the fluorescence intensity and the observed rate constant (k_{obs}) were obtained by a linear least-squares fit of the semilogarithmic plot of Ln F0/F vs time.Photo-oxidation of Trp was used to determine $^1O_2$production by pro-oxidant activity of "jaceidin", usingbengal roseas positive control. The solution was irradiated under continuous oxygen flow,and a 150W lamp wasused as source of illumination (380–780 nm).Riboflavin (Rf) hasa triene structure and many double bonds be able to react with$^1O_2$; at the same time Rfits photo-degradated for his own productionof this excited oxygenspecies [6]. This ambiguous behavior allowsus to determinatethe antioxidant effects of "jaceidin" against to$^1O_2$.Under irradiationriboflavin content decreased considerably dependingof the illumination time. The negative control sample containing only riboflavin. The presence of "jaceidin" in riboflavin solutions reduced photo-degradation of riboflavin, and the rate of degradation was slower than negative control. Toestimate the capacity of "jaceidin"to protect riboflavin facingof photo-degradation, we used ascorbic aciddue to great capacityas scavenger of reactive oxygen species.About Trp photolysis, we demonstrated that "jaceidin" showsa barely detectable pro-oxidant activity. This research allows us to propose a new approach in the classification of natural antioxidants scavenger's free radicals. Therefore, it's necessary to evaluate a large number of antioxidants, already usedin food industry, beverages, supplements, and personal care/cosmetics, or find new ones in order to use real antioxidants compounds.

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P28- Potassium iodide enhancer effect on the photodynamic inactivation of microorganisms sensitized by cationic BODIPY derivatives

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Photodynamic inactivation (PDI) of microorganisms has been proposed as an alternative therapy to eradication of microbes. PDI is founded in the administration of a photosensitizer, which is preferentially bound to microbial cells. The subsequent aerobic irradiation of the affected area with visible light produces cell damages that inactivate the microorganisms due tolocalized formation of reactive oxygen species (ROS). In this sense, two new cationic borodipyrromethenes (BODIPYs: 1,3,5,7-tetramethyl-8-[4-(*N*,*N*,*N*-trimethylamino)phenyl]-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene **1** and 8-[4-(3-(*N*,*N*,*N*-trimethylamino)propoxy)phenyl]-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene **2**) were investigated as photosensitizing agents for the PDI on *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*, in the absence and in presence of potassium iodide (KI).*In vitro* experiments indicated that both BODIPYs were rapidly bound to microbial cells at short incubation periods. Also, fluorescence microscopy images showed the green emission of the BODIPYs bound to microbial cells. Photosensitized inactivation improved with an increase of the irradiation times. After 15 min irradiation, a complete eradication of *S. aureus* was obtained with 1 μM photosensitizer. A reduction of 4.5 log in the *E. coli*and *C. albicans*viability was found using 5 μM photosensitizer and 30 min irradiation. On the other hand, the addition of KI was investigated on photoinactivation at different irradiation periods and salt concentrations. A smaller effect was observed in *S. aureus* because the photosensitizers alone were already very effective. In *E. coli*and *C. albicans*, photokilling potentiation was mainly found a longer irradiation periods.

In solution, an increase in the formation of the BODIPY triplet states was observedwith the addition of the salt, due to the effect of external heavy atom. The greater intersystem crossing in the presence of the salt,together with the formation of reactive iodine species induced by BODIPYs may be contributing to enhance the inactivation of microorganisms. The results show that the photosensitized action of BODIPYs **1** and **2**, combined with the non-toxic nature of KI, allows an efficient inactivation of the microorganisms.

P29- Photodegradation of Phenol adsorbed on novel magnetic montmorillonite coated with bio-based substances generated from urban solid waste

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Petrochemical and oil refineries, wood processing, plastics, rubber, textile, coating and leather industries' wasterwaters can hold in different phenolic compounds. Those kind of substances are potentially toxic or cancinogenic, being a serious threat to the biosphere.[1] Hence, for safe disposal of these wastes it is imperative to remove those hazardous compounds. In order to develop alternative methods of phenols removal from water, a new sorbent material was tested using phenol as model pollulant.

Recently, it has been considered the application of humic substances (HS) as additives in contaminated water treatment.[2] Humic Substances, are good metal complexing agents and, in turn, can act as organic compounds' adsorbents.[3] Additionally, HS photolysis leads to the formation of several reactive species including free radicals, reactive triplet states, hydroxyl radicals, singlet molecular oxygen and hydrogen peroxide, which are involved in aquatic photochemistry.[4] All these facts can explain the beneficial effect of HS incorporation in photochemical degradation treatments of pollutants.[5][6] Besides, urban solid waste breakdown produces substances with composition and structures similar to HS, which are known as soluble bio-based substances (BBS).[7] In this context, our research group have synthesized Fe_3O_4 nanoparticles (NPs) coated with BBS in order to employ them as low-cost nanoadsorbent for the removal of pollutants in wastewaters.[8]

In this work, hybrid materials: magnetite- BBS -montmorillonite were prepared and characterized by different techniques (FTIR, DRX, measurements of specific surface area by nitrogen and water adsorption, zeta potential zeta, and magnetization). In order to develop alternative methods of phenols removal from water, this new sorbent material and photosensitizer was tested using phenol as model contaminant. The results obtained show that urban solid wastes can be recycled in the synthesis of hybrid materials for the removal of phenolic pollutants from wastewater. Under visible light irradiation, the BBS behave as photosensitizer generating phenol photodegradation.

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P30- Copper clusters as novel photocatalysts for aerobic oxidation of arylboronic acids and esters under ecofriendly conditions.

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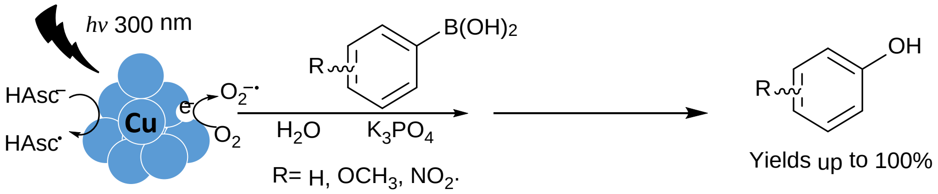
Metal clusters can be defined as metal atom aggregates with sizes between 1 to 2 nm.[1] For these novel materials high chemical stability and novel properties including surprising high catalytic performances have been described.[2] Up to now, copper clusters (CuCLs) have attracted less attention than gold and silver clusters. However, due to their low cost and unique optical and catalytic properties different publications have recently reported the synthesis and characterization of CuCLs.[3] Besides, previous reports have demonstrated that photocatalytic behavior of CuCLs would be similar to the accepted one for photoactive semiconductors (SCs),[4] which involves the generation of reactive oxygen species, such as $O_2^{\bullet -}$, $HOO^{\bullet}$ or $HO^{\bullet}$, produced by the reaction between adsorbed water, molecular oxygen and photoelectrons when they migrate to the semiconductor´s surface.

Recently, we have described the use of water soluble quantum dots for the oxidation of arylboronic acids and esters to obtain their corresponding phenols. In this investigation, the visible light photogenerated superoxide anion promotes the ipso hydroxylation of different arylboronic acids and esters.[5]

Herein, we report for the first time the photocatalytic oxidation of different arylboronic acids and arylboronic esters using CuCLs under UV-A irradiation (Scheme 1). The CuCLs were synthesized and characterized for López-Quintela group (Nanomag Laboratory, Research Technological Institute, University of Santiago de Compostela, Spain). Under optimized conditions; we further studied the reactivity scope of the reaction. This methodology proved to be compatible with electron donors and electron withdrawing substituents and the corresponding phenols from arylboronic esters were also obtained in good yields (48–87 %). On the other hand, arylboronic acids rendered phenols in very good to excellent yields (92–100%).

Scheme 1:



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P31- Nanosystems based on hydroxyapatite as fluorescent vehicles for drug delivery

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The most important constituent of bones and teeth is hydroxyapatite, a biomaterial capable of supporting osteogenesis and osteoconductivity. The synthetic hydroxyapatite (Ap), $Ca_{10}(PO_4)_6(OH)_2$, presents chemical composition similar to the majority mineral phase of the hard tissues [1]. Ap-based nanosystems can be functionalized to be used in controlled drug delivery [2], which seeks to replace the inefficient bolus administration of drugs especially in the treatment of bone diseases [3].In this work we propose to develop nanospheres formed by liposomes coated with an Ap layer, which provides them with stability, stiffness and affinity in the biological media [4-5]. The Ap-coated nanoliposomes will serve as vehicles for the specific administration of drugs encapsulated in their interior and will be superficially modified with bone tissue recognition molecules and fluorophores. The latter, gives Ap-coated nanoliposomes fluorescent capacity for their use as optical sensors.

To that purpose, 1,2-Dioleoyl-sn-glycero-3-phosphate (DOPA) liposomes containing the fluorescent antibiotic levofloxacin (Lx), were prepared by the extrusion method using commercial ethanol as solvent. Subsequently, they were coated with Ap following the procedures reported in the literature[6] and then the CV was anchored to its surface through amide bond. The CV allows tracking of the nanoliposome and has a different emission spectrum than the Lx, so that the presence of each compound can be determined by fluorescence techniques.

TEM images (see Figure 1), show well defined coated nanoliposomes of approximately 100nm size. The fluorescence spectrum of the nanoliposomes depict maxima at 420 and 624 nm assigned to Lx and CV, respectively, as shown in Figure 2. Encapsulation of Lx was evidenced through steady state and time resolved fluorescence studies. The anchorage of the fluorophore to the surface is supported by the fluorescence of CV-anchored to the liposomes, which is 4 nm blue shifted compared to solution-free CV and the results of electrophoretic mobility ($x10^{-4}$ cm^2/Vs) before (-2.0±0.2) and after (-0.8±0.1) the CV addition.

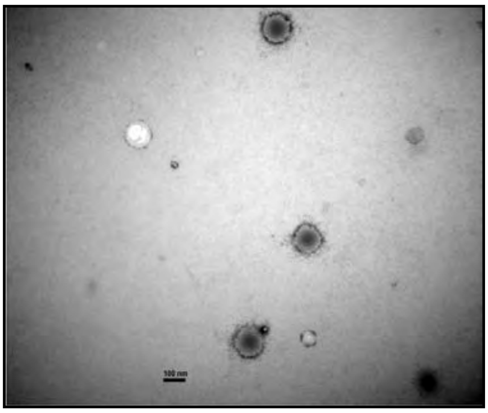

Figure 1. TEM image of liposomes. The black line stands marks 100 nm.

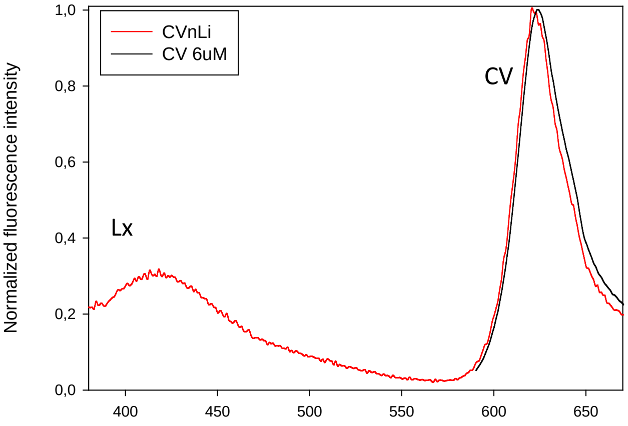

Figure 2. Red lines stand for the fluorescence spectrum of CV anchored to Lx encapsulated nanoliposomes and black curve for 6µM CV in an aqueous solution.

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P32-Photophysical properties of fac-Re^{I}(CO)$_3$(pterin)(H2O) complex. Photochemically and thermally induced redox reactions.

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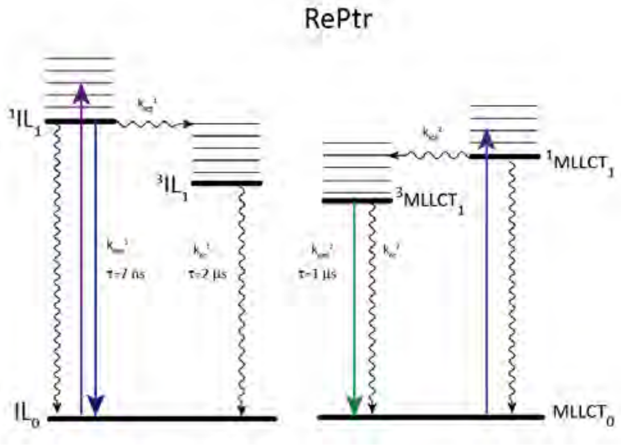
In this work, we present a whole and deep study on the thermal redox and the photophysycal and photochemical reactions of a tricarbonyl Re(I) complex coordinating Ptr[1] (RePtr).

The photophysical study of the RePtr complex realized in this work allowed to identify the nature and characteristics of its excited states. In addition, some intermediates and photo-products have been identified. In aqueous solutions, the complex fluorescence is attributed to the emitting ^{1}IL state. In MeCN, however, the luminescence was ascribed to an interplay between ^{1}IL and ^{3}MLLCT states. The quantum fluorescence yield of the complex is much lower than its free ligand. This result is in good agreement with the theoretical calculations TD-DFT performed on the ligand and the complex, indicating a higher contribution of MLLCT than ^{1}IL states to the electronic transitions that are populated by excitation at 350 nm.



Flash photolyses results agreed, either in aqueous or MeCN solutions, helped to identify the naterure of the generated excited states. In aqueous solutions the ^{3}IL state of Ptr in the Re-complex was detected. However, in MeCN solutions, flash photolyses experiments showed spectral features of the generated transients more consistent with the emitting ^{3}MLCT. The deactivation of ^{3}MLCT by O_2 leads to the formation of $^1O_2$ with a low quantum yield. No formation of $^1O_2$ in D_2O was detected, possibly due to a very low ^{3}IL formation quantum yield. LIOAS spectroscopy confirmed that this complex released to the medium all the absorbed energy as prompt heat after laser excitation at 355 nm either in H_2O and/or MeCN.

The reduced transient spectrum generated by flash photolysis is in good agreement with the published spectra of the reduced ligand radical [2].

Pulse radiolysis experiments under oxidizing and/or reducing environments were performed in aqueous solutions of the Re complex. By performing an analysis by MCR-ALS, it was possible to identify the contribution of three species. The first intermediate was assigned, by spectral similarity, to the semireduced radical of the free ligand [3,4]. This spectrum also agrees with the spectrum found for the reduced transient generated by flash photolysis. The proposed reduction product is the complex Re(CO)$_3$(7,8-PtrH$_2$)(H$_2$O). The oxidized transient spectrum was also obtained by pulse radiolysis, this compares very well with those published for Re^{II}, leading us to propose oxidation in the metal core as the reaction product of the transient under oxidizing conditions.

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P33-Visible-light Assisted Cu(II) Reduction Employing Organic Dyes: Applications in the Triazole Synthesis

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Over the last decades, interest in the synthesis of 1,2,3-triazoles has significantly increased.[1] Due to their particular properties, they are increasingly employed in several areas of chemistry such as new drug discovery, biochemistry, dendrimers, polymer chemistry, and materials science. Currently, the copper-catalyzed azide-alkyne cycloaddition (CuAAC) is the most commonly used method for the synthesis of 1,2,3-triazoles.[2-4] It is widely demonstrated that Cu(I) is the catalytically active species which leads to the exclusive formation of 1,4-disubstituted 1,2,3-triazole in CuAAC reactions.[5]

In the present work, we describe the use of organic dyes as a Cu(II) reducing agent by photoredox reactions which promote the Cu(I) formation, and its use as a catalyst for the synthesis of triazoles (Figure 1). Several organic dyes and Cu(II) sources were tested during optimization reaction, as well as control reactions were performed in order to verify that dye, Cu(II) and visible ligth must be present at the same time to form the cataliticly active specie Cu(I). To study the reaction scope, benzyl, phenacyl, alkyl and aryl azides, as well as aryl, and alkyl terminal alkynes were tested under optimized conditions with good to excellent isolated yields.

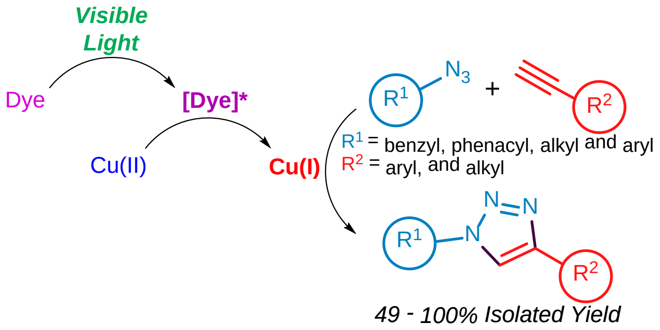

Figure 1. Synthesis of 1,4-disubstituted 1,2,3-triazoles *via* visible-light promoted CuAAC reaction.

This simple and environment friendly methodology employs water as a renewable and non-toxic solvent; amount of catalyst precursor is much less than conventional methodologies (TON = 710). Metal and solvent can be recycled for up to three times without a considerable loss of efficiency, visible light through LED is used, which is inexpensive and safer that methodologies which employ UV irradiation to promote Cu(II) reduction and additives are not required. In addition, an efficient one-step one-pot procedure was designed and carried out, avoiding synthesis and handle of organic azides that many times could be unsafe.

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P34-Synthesis and photophysical characterization of substituted Tröger´s bases.

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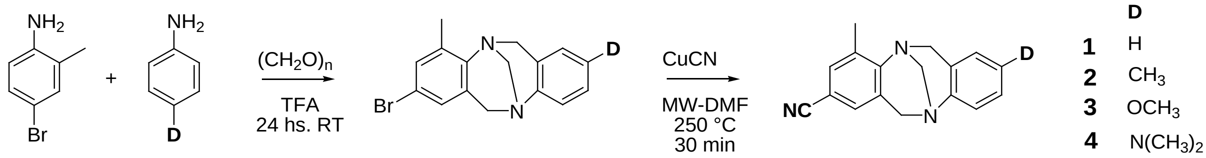
Synthetic dyes are generally made up by an electron acceptor (A) and an electron donor (D) group coupled by π or σ bridges. The σ bridge allows only the adiabatic coupling between A and D, a property that was advantageously used for the design of diodes and photodiodes at the molecular level.[1] We report herein the synthesis and characterization of a series of new chromophores based on a methanodibenzo[*b,f*][1,5]diazocine bridge (σ_T), whose properties as charge carriers have not been yet explored. These chromophores, also known as Trögers bases (A-σ_T-D), were synthetized as shown below. Trögers **1-4** have a common acceptor (A= CN) and a series of D with increasing electron donor capacity.



The brominated precursor of **1-4** were synthetized by reacting 1:1:4 molar mixtures of 4-bromo-2-methylaniline, the corresponding *p*-D-aniline and *p*-formaldehyde, respectively, using trifluoroacetic acid (TFA) as solvent. After 24 hours, reactions were quenched with ammonium hydroxide and the obtained precipitates purified by column chromatography to give the products in 30-40 % yields.[2] The microwave-assisted cyanation of the brominated diazocines to yield **1-4** was carried-out using an methodology optimized in our research group. Efficient cyanation was observed using CuCN in dimethyl formamide (DMF) and irradiating with 850W for 30 minutes at 250 °C. After reactant´s conversion was completed, products were extracted with ethyl acetate, dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Yields were excellent to very good: 99 -77 %. Compounds **1-4** were characterized by ^{1}H- and ^{13}C-NMR and IR spectroscopies.

The energy of **1-4** absorption ($h\nu_A$) and emission ($h\nu_E$) maxima, fluorescence quantum yields (φ_f) and emission lifetimes (τ_f) were evaluated in a series of aprotic solvent covering a wide range of solvent polarity (ε = 2-37). **1-4** show absorption spectra typical of substituted aromatic compounds. **1-3** show a forbidden transition ($\varepsilon \sim 4000\ M^{-1}\ cm^{-1}$) centred ~ 280-290 nm and a much intense transition at ~ 240 nm. In the case of **4**, the forbidden transition is red-shifted (~325 nm). $h\nu_A$ slightly shift to lower energies with the increase of solvent polarity. **1-4** are scarcely fluorescent compounds. φ_f, τ_f and $h\nu_E$ strongly depend on D and on the solvent polarity. The change of the dipolar moment ($\Delta\mu$), associated to the $S_1 \rightarrow S_0$ transition, were calculated from typical Lippert-Mataga plots. Values of $\Delta\mu$ = 7.8, 8.3, 9.2 and 12.4 D were obtained for **1-4**, respectively. Results suggest that excitation of the Tröger´s base leads to the formation of charge transfer (CT) states with partial (**1-3**) and full (**4**) charge separation. Interestingly, the diazocine bridge (σ_T) plays an active role in the CT process, conclusion that is in fully agreement with TD-TFD theoretical calculations performed on the structures of **1-4**.

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P35- Photohydrogenation of polycyclic aromatics hydrocarbons

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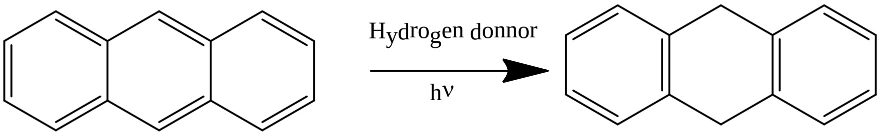
Hydrogen is one of the most promissing energy source in near future. Besides storing the fuel, controlling the hydrogenation process will make the hydrogen economy real in a short term. Polycyclic aromatic hydrocarbons (PAH´s) are a class of organic compounds with many different chemical uses but also, potentially as hydrogen storage molecules. Although the existence of different methodologies to hydrogenate PAH´s, thermodinamic limitations are common to all of them and demand the use of metal catalyst and high hydrogen pressions [1] in order to occurs. Therefore, new alternative hydrogenation technologies emmerge with huge importance for the next generation.

In this context, our group has been studying metal free hydrogenation of PAH´s in excited state using different hydrogen sources in absence of metal catalyst. In this study we show the mechanisms of anthracene photohydrogenation in the presence of sodium isopropoxide, 1,4-cicloexadiene or triethylamine as hydrogen donnors.

Reactions were conducted using a 300 W Xe lamp at 25 ^{o}C and anthracene : hydrogen donnor ratio of 1:20 (mmol) in deaerated acetonitrile. By GC-MS analysis, the main product of the anthracene hydrogenation, for the three cases, was 9,10-dihydroanthracene, as follow.



Conversions reached up to more than 70 % in 120 minutes using sodium isopropoxide as hydrogen source. The LFP experiments showed that hydrogen transfer occurred at the first triplet state for anthracene and the quenching rates for sodium isopropoxide (Figure 1), 1,4-cicloexadiene and triethylamine were: 3,18x10^{6}, 2,17x10^{5} and 8,34x10^{5} L.mol.*s*$^{-1}$, respectivelly. To the best of our knowledge it is the first time that hydrogen transfer from 1,4-cyclohexadiene to a PAH is studied in literature.

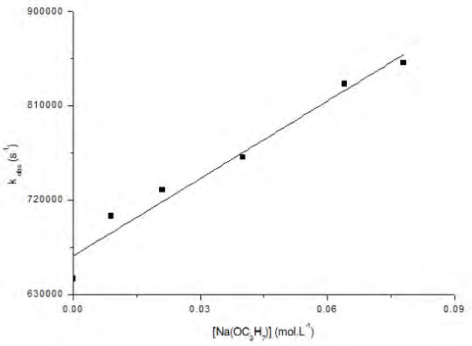


Figure 1: Stern-Volmer for anthracene using sodium isopropoxide as supressor.

Acknowledgments: CNPq and Chemistry Institute UFRJ.

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P36- Asphaltene structure by static and dynamic quenching

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Asphaltene is the fraction of petroleum that, by definition, is insoluble in linear alkane, such as pentane or heptane, and soluble in toluene. This fraction is responsible for problems in petroleum extraction, transportation, and refining due to the easy of aggregation, which reduces flow and increasing downtime for cleaning. [1]

One of the most controversial point on asphaltene chemistry is related to the structure of such fraction. In literature, two different models can be depicted: the archipelago, in which the components are part of sub-structures formed by aromatic cores joined by methylene bridges (containning heteroatoms) and, [2] and the island, in which the aromatic cores are not joined, but they can interact by intermolecular forces. [3].

Although substantial results in literature, most of the papers worked with concentrations above asphaltene aggregation limit of 50 mg/L or non-appropriate analysis technic. So, the studies do not bring a detailed information on asphaltene composition and structure without interference of aggregates.

This study evaluates the structure and aromatic components of asphaltene by following the asphaltene fluorescence quenching (below 50 mg/L) by probes like CH_2I_2, phenanthrene, crysene, tetraphenylporphyrin and the quinoline complexes of Al^{3+}, $Ga^{3+}$and In^{3+}. Our results indicate three main observations: (1) from CH_2I_2 quenching experiment the asphaltene fluorescence was quenched mainly from 250-400 nm; (2) flat molecules quenches asphaltene preferentially by static mechanism, otherwise, dynamic quenching of asphaltene were found whith non-planar molecules and, (3) the quenching rate of asphaltene is directly related to the first excited singlet energy of the quencher. In the light of our results we conclude that even in concentrations below 50 mg/L asphaltene possess a tridimensional structure with aromatic molecules distribution showing from to 4-6 condensed aromatic rings.

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P37- Gold nanoclusters conjugated with bovine serum albumine as a novel photosensityzer agent and fluorescent probes

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Noble metal nanoclusters (NCs) typically consist of several to tens of atoms. They are <1 nm in size, and their properties are governed by their subnanometer dimensions. This size regime is comparable to the Fermi wavelength of the conduction electrons [1]. Due to their ultrasmall size, unique molecule-like optical properties, and facile synthesis gold nanoclusters have been considered very promising photoluminescent agents for biosensing, bioimaging, and targeted therapy. Yet, interaction of such ultra-small nanoclusters with cells and other biological objects remains poorly understood. Therefore, the assessment of the biocompatibility and potential toxicity of gold nanoclusters is of major importance before their clinical application [1,2].

BSA-Au NCs were synthesized according to a reported "green" synthetic route [3,4]. The red emitting Au NCs were prepared by adding aqueous $HAuCl_4$ solution (5 mL, 10 mM, 37°C) to BSA solution (5 mL, 20 mg/mL, 37° C) under vigorous stirring. NaOH solution (0.5 mL, 1 M) was introduced 5 min later, and the reaction was allowed to proceed under vigorous stirring at 37° C for 12 h. The deep brown solution of Au NCs emit intense red fluorescence under UV light (365 nm), which can be observed by the naked eye.

These BSA-Au NCs were characterized by TEM, DLS, zeta potential measurements, XPS and UV-visible spectroscopy. Fluorescence spectra were examined to detect the optical properties of BSA-Au NCs under an excitation wavelength of 470 nm and the fluorescent BSA-Au NCs showed an emission peak at 650 nm. The photoluminescence quantum yield of the BSA-Au NCs was measured to be ~6%, which was calibrated with fluorescein (λexc = 470 nm). These physicochemical properties of the Au NCs indicated that we had successfully synthesized the red-fluorescent BSA-Au NCs with 25 gold atoms [4]. In addition, the fluorescence decay of the emission showed that the dominant fluuorescence lifetime of BSA-Au NCs was ~2 μs, these fluorescence lifetime results are considerably lasting compared with those of traditional fluorescent dyes [5]. Therefore, these BSA-Au NCs may offer a great opportunities for fluorescence lifetime imaging in the future. The ability to generate reactive oxygen species from the BSA-Au NCs was studied by indirect methods.

In order to analyze its potential application as photosensitizing agents in photodynamic therapy (PDT), cytotoxicity studies were carried out in the dark and under irradiation with different light sources. For example, the MTT assay in HeLa cells shows differences in the toxicity of this system when the cell culture is irradiated with a white light lamp with respect to the control maintained in the dark, which allows to think about its application in this type of therapy.

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P38- Visible-light mediated installation of halogen functionality into aromatic systems

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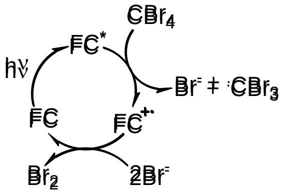
The development of new methods for introducing halogens into organic compounds has constantly attracted many research groups. Halogen substituted compounds are important building blocks in organic synthesis for conversion and introduction of more valuable functional groups by transition metal catalysis[1] and nucleophilic substitution.[2] Furthermore, the interaction of halogen bonds with proteins or small molecules provide modulated physical and chemical properties such as lipophilicity and thermal/oxidative stability.

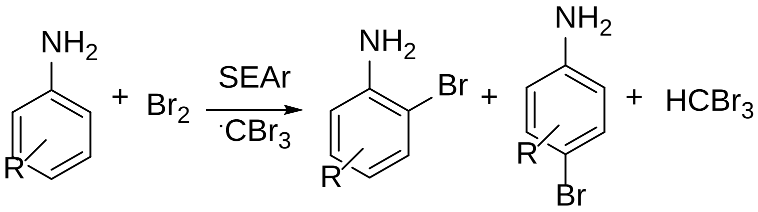
The introduction of halogen functionalities into an aromatic system is a well-established method in organic chemistry. Most commonly activated aromatic rings are converted directly through reaction with excess of the diatomic halogens. However, this method suffers from critical drawbacks with handling of highly hazardous and volatile halogens and poor regioselectivity. Up to date, the most used bromination procedures involves the use *N*-Bromosuccinimide, transition metals catalyst or solutions of molecular bromine (Br_2), these methodologies carry a high economic cost, high toxicity and requires the use of heat sources.

In order to solve the above mentioned problems, visible-light photoredox catalysis has arisen as alternative. In the present report, we propose the bromination of anilines using organic photocatalysts and carbon tetrabromide (CBr_4) as a source of bromine. *"in situ"* Elemental bromide formation is possible using photocatalysts (FCs) such as Ru(bpy_3) Cl_2 and Eosin Y (EY) (Scheme 1).[3]



Scheme 1

Under this contribution, several bromo anilines and brominated heterocycles from activated substrates could be obtained by electrophilic aromatic substitution (S_EAr) (Scheme 2). This methodology provided an alternative synthetic path with an advantage of avoiding toxic, liquid bromine and expensive transition metal catalyst.



Scheme 2

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P39- Interaction of arylmethylene thiohydantoins with DNA

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In many fields of chemistry and molecular biology, DNA detection is essential in order to study different phenomena. This can be achieved by dyes techniques employing fluorescent probes. The most commonly used dye is ethidium bromide (EtBr).[1] It is an intercalating agent which is also known for its toxicity and mutagenicity. So, the development of fluorescent probes capable to interact with DNA has attracted much attention.[2-3] Several ligands interact with DNA through covalent and electrostatic binding or intercalation. Compounds with rigid and planar structures are good candidates for DNA intercalation. In addition, some of these compounds are used in chemotherapeutic treatments to inhibit DNA replication in rapidly growing cells.[2]

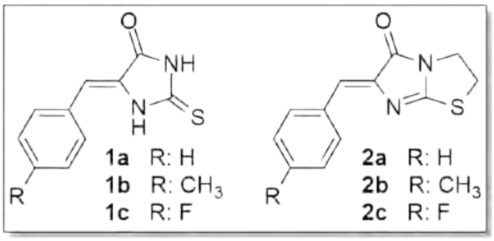

Figure 1: Studied thiohydantoin derivatives.

In this work, we synthetized thioxoimidazolidin-4-one derivatives (TH, **1a-c** and **2a-c**, *figure 1*), studied their luminescence properties and evaluated the possibility of their application in the detection of double stranded DNA (dsDNA). These compounds are good candidates as fluorescent probes due to their planar structure and the heteroatoms that may form hydrogen bonds.

The fluorescent profile was examined in the absence and presence of fish dsDNA. Solutions of the samples were prepared in DMSO rising a final concentration of 0.3 mM. Ethidium bromide was analyzed at a lower concentration of 15μM due to its high fluorescence emission. All the analyses and incubation times were performed at a controlled temperature (30°C). The comparative results for the unsubstituted compounds (**1a** and **2a**) are shown in *figure 2* together with the spectrum for ethidium bromide at the concentration needed to reach similar emission intensities ([TH]/[EtBr]=20).

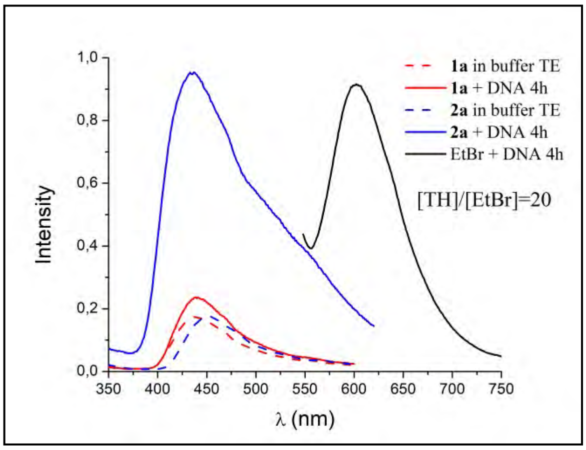

Figure 2: Fluorescence spectra of studied compounds in buffer TE and in solution of dsDNA 0.029%P/P.

Compound **1a** presents a rather modest fluorescence emission which somewhat increases after incubation with dsDNA. In contrast, **2a**, whose fluorescence emission is comparable to **1a**, rises 20 times after 4 h of incubation with dsDNA. As it is possible to see, compound **2a** interacts better with DNA because it has a bigger planar structure. In addition, compounds **1** present tautomerism which is a well-known mechanism of fluorescence deactivation.

In spite of the higher concentration of the fused-thiohydantoin derivatives compared to ethidium bromide (ratio of concentrations ~20), we believe that the presenting compounds could perform as fluorescent probes because their emission appear well within the visible region besides of its reduced toxicity.

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P40- Tropospheric degradation by solar photolysis of biogenic unsaturated aldehydes

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Volatile Organic Compounds (VOCs) emitted from vegetation often referred to as biogenic volatile organic compounds (BVOCs) are considered to be the main source of reactive species in the troposphere[1]. Aldehydes play an important role in atmospheric chemistry since they are recognized as important key precursors in the formation of tropospheric ozone and OH radicals[2] and are also potential prolific sources of secondary organic aerosols through their reactions with atmospheric oxidants and photolysis.[3]

Aldehydes are ubiquitous gaseous chemical constituents in the atmosphere and are emitted by a variety of biogenic sources.[2]

In the troposphere aldehydes can be photolyzed[2] and will also be subject to reaction with the atmospheric oxidants OH radicals, NO_3 radicals and O_3 molecules and also Cl atoms. The combination of the photodissociation of aldehydes and reaction with the atmospheric oxidants represents, in many cases, an important source of free radicals in the lower atmosphere which can significantly influence the atmospheric oxidation capacity.[2]

We present here, a photochemical study in the actinic region of a series of unsaturated aldehydes as: *(E)*-2-heptenal ($CH_3(CH_2)_3CH{=}CHC(O)H$), *(E)*-2-octenal ($CH_3(CH_2)_4CH{=}CHC(O)H$) and *(E)*-2-nonenal ($CH_3(CH_2)_5CH{=}CHC(O)H$) of atmospheric interest, since as mentioned above they are emitted by different types of vegetation.[1]

Photolysis of the aldehydes follows first order kinetics and can be represented by:

$$\text{Aldehyde} + h\nu \rightarrow \text{products}, \qquad j$$

where j is the photolysis rate coefficient. We report the photolysis rate coefficients of these VOCs by direct photolysis of the sun using a 80 L teflon bag coupled to Gas Cromatography with Flame Ionization Detector (GC-FID) as detection system. Values of j(*(E)*-2-heptenal)= $(3.4 \pm 0.4) \times 10^{-5}\ s^{-1}$, j(*(E)*-2-octenal)= $(1.5 \pm 0.5) \times 10^{-5}\ s^{-1}$ and j(*(E)*-2-nonenal)= $(4.3 \pm 0.5) \times 10^{-5}\ s^{-1}$ were determined The photolysis processes of these aldehydes are very important with tropospheric lifetimes of 6 to 18 hours which would indicate that the photolysis reactions of these long chain aldehydes could compete with the OH-radical-initiated reactions. In general mechanistic studies of short chain aldehydes demonstrate that the photolysis channel has a yield of 50% and the remaining 50% is the reaction pathway with OH radical during the day.[4]

Therefore, we can consider that the atmospheric sinks of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal in the atmosphere during the day is the reaction with OH and solar photolysis. The photolysis of these unsaturated aldehydes in the atmosphere is expected to be generate several species including 2-hexenal, 2-heptenal, 2-octenal, CO and HOx radicals.

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P41- Paracetamol degradation from aqueous solutions: advanced oxidation methods

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A pollution problem that is currently affecting surface water, wastewater and even human consumption is pollution by non-polluting substances, emerging pollutants, pharmaceutical residues, hormones, personal care products and sunscreens Fragrances, flame retardants as compounds Polybromates, illicit drugs, among others. These contaminants have poor biodegradability and are difficult to eliminate using conventional water purification methods [1]

It is for this reason that alternative methods are used for the degradation of these pollutants, such as advanced oxidation methods.

Acetaminophen or paracetamol (N- (4-hydroxyphenyl) acetamide) is widely used as an analgesic and antipyretic. In Chile, it is bought without a prescription. This compound is considered an emerging pollutant since a toxic metabolite is generated in its enzymatic oxidative action in the liver. In U.S.A. Paracetamol was found in natural waters; It has also been detected in European effluents from Korea, Spain and France [2]

In this work, a series of experiments have been developed using as advanced oxidation treatments a mixture of Heterogeneous Photocatalysis and ozonization. Performed in a closed tubular reactor, which contains a UV-C lamp in the center, and is filled with clean raschig rings or with TiO_2 (according to experiment conditions) in addition to a bottom entry that allows the ozone to bubble up to Throughout the solution.

The volume to be treated in each experiment was 2.0 [L], maintaining the pH of the solution (5.6), and its initial concentration (50 [ppm]), varying in each experiment the use of TiO_2 impregnated rasching rings, irradiation 254 [nm] and the use of hydrogen peroxide.

Each of the degradations of the drug has been analyzed by a Flexar-PerkinElmer HPLC UV equipment.

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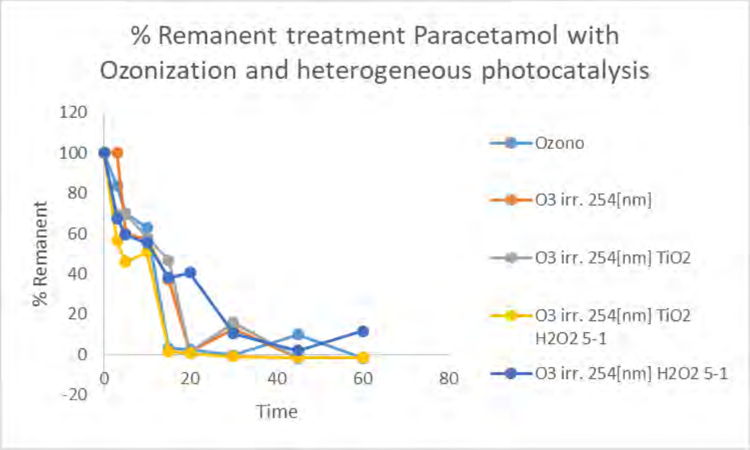

Fig 1: Graph % remaining treatment Paracetamol with Ozonization and heterogeneous photocatalysis under different conditions

Some conclusions: A) The best degradation time was obtained with the treatment of ozone with irradiation 254 [nm], TiO_2 and hydrogen peroxide in molar relation with the drug 5-1, achieving total degradation at 20 min of treatment B) The less efficient treatment is with ozone irradiation 254 [nm] and hydrogen peroxide in molar ratio with the drug 5-1, which at 60 minutes of treatment records a remaining 11.44%

Acknowledgments: The authors thank the DGIP- UTFSM for their support through the Project N°. 23.15.52.

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P42- Strange Kinetics in the Photoreaction of 3-Phenyl-quinoxalin-2-ones with N-Phenylglycine.

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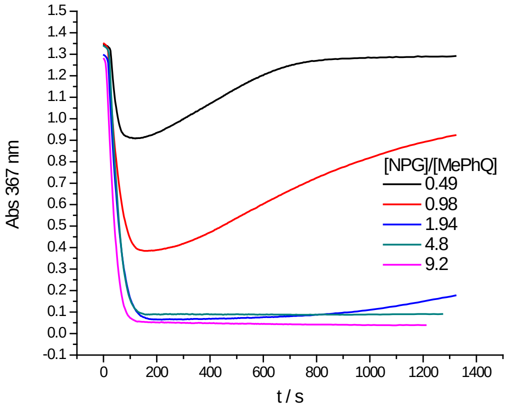
The 3-phenyl- derivatives of quinoxalin-2-ones, **3-PhQ**, are photoreduced efficiently by amines by a stepwise transfer of electron-proton-electron, resulting in a metastable photoproduct that revert quantitatively to the starting quinoxalin-2-one [1,2]. In the photoreaction with *N*-phenylglycine, **NPG** strange kinetics that depends on the molar ratio NPG/3-PhQ, as shown in Fig 1, can be observed. It is known that NPG after a single electron transfer undergo a fast decarboxylation that generates the α-aminoalkyl radical $PhNHCH_2\bullet$ showing transient absorptions below 320 nm. [3]



The study of these photoreactions by steady state and flash photolysis allow us to propose a reaction mechanism similar to those reported previously for the photoreduction by amines.

We thanks FONDECYT Grant N° 1150567 for the financial support.

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P43-Metal nanoparticles concentration effects on the photophysical properties of molecular and supramolecular probes.

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Nowadays, it is widely accepted metal nanoparticles (NP) affect the photophysical and photochemical performance of molecules located close or in contact with the metal surface in different ways. Either quenching or enhancement of their properties can be produced, and factors affecting these phenomena are NP size, composition, shape as well as distance of the molecule from the surface [1-2]. Although, the mentioned properties variations are continually explored to improve molecule sensing, reports on the effect of nanoparticle concentration on the photophysical properties such as fluorescence are still scarce.

On the other hand, due to the environmental implications NP can have, in the last years it has been an increased interest on developing analytical methods oriented to the detection of NP. In this frame, our aim is to explore the NP concentration dependance of the photophysical properties of molecular probes and supramolecular complexes as an strategy to detect metal nanoparticles in mixtures.

In this work we selected Rhodamine B and 6G (RhB and Rh6G, respectively) as molecular probes and carbazol@cyclodextrins (CZL@CDs) as the supramolecular systems; and colloidal AgNP (citrate, gallic acid or stabilized by a gemini surfactant) and AuNP (citrate stabilized) as the tested NP. We evaluated the effect on the fluorescence of RhB, Rh6G and CZL@CDs of the presence of different NP at different concentrations with or without pH control. A comparison between all the systems will be discussed.

Acknowledgments
We want to thank Dr. Mariana Fernandez and Lic. Erica Pachón Gómez for providing the gemini surfactant. We also would like to thank ANPCyT, SECYT-UNC and CONICET for funding this project.

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P44-Design and synthesis of fluorescent ligands for selective detection of a target protein

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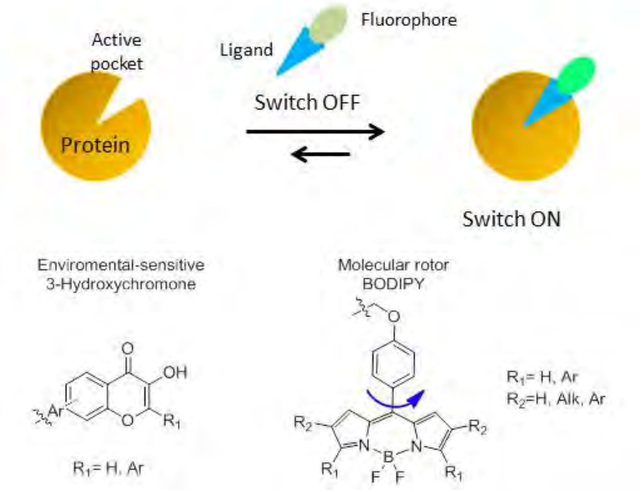
Screening is a key tool to find promising compounds in a large set able to modulate biological activity of specific therapeutic targets with the hypothesis that this will provide new drug leads[1]. Proteins are some of the major therapeutic targets. The relevant assays used as a sifting process must be reproducible, reliable, and robust. Fluorescent-based techniques are simple, economic, and sensitive methods widely used in screening. An active pocket of proteins/enzymes is used as target to design selective ligands/inihibitors. Such protein–ligand interactions have been utilized to develop selective protein sensing/imaging systems. The key issue represents how to transduce the ligand/protein recognition into readable detection signals. Fluorescence switch-on can be achieved upon the binding of the fluorescent probes to the active ligand-binding domain of the target protein [2]. Most of the ligand fluorescent switch-on probes are designed for monitoring enzyme activities so the design of fluorescence switchable probes for non-enzymatic protein targets is highly desirable.

The fluorescent probes can be synthesized by conjugating a fluorophore with a protein-specific ligand. We focus on two representative detection concepts: (i) environmentally-sensitive probes exhibiting very weak fluorescence in a polar and/or protic environment but strong fluorescence in a hydrophobic surrounding, and (ii) molecular rotor probes, undergoing intramolecular charge transfer upon irradiation, relax via the nonradiative torsional relaxation pathway, and are thus sensitive to changes in viscosity.

Our model system consists in 3-hydroxychromone (3HC)[3] as a small and highly environmentally sensitive fluorophore and BODIPY[4] as molecular rotor, which are conjugated to benzenesulfonamide, a ligand for carbonic anhydrase II (hCAII) as a target protein. HC derivatives show dual-color emission and thus a ratiometric response due to Excited-State Intramolecular Proton Transfer (ESIPT) and therefore constitute very versatile and sensitive probes of environmental properties such as polarity and hydrogen-bonding capacity.



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P45-Effect of light on *Ralstonia solanacearum* physiological features involved in host plant colonization

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Light perception in living organisms is achieved by photoreceptor proteins, which trigger signal transduction cascades that regulate light responses. LOV (*Light, Oxygen* or *Voltage*) photoreceptors are flavin-binding proteins using flavin mononucleotide (FMN) as chromophore [1-2]. *Ralstonia solanacearum* (Rso) is a soil-borne pathogen responsible for bacterial wilt, a severe disease that affects many economically important crops such as potato and tomato [3]. Analysis of the Rso GMI1000 genome sequence revealed the presence of one gene encoding a putative transmembrane LOV protein: *rsp0254* [4]. The aim of this work was to study the effect of light in the Rso physiology.

We evaluated the bacterial growth of Rso GMI1000 in liquid medium under white light, blue light and darkness. Several physiological parameters involved in the first stages of Rso infection of the host plant were determined in the different light conditions. Bacterial motility mechanisms, such as swimming and twitching, were evaluated, and the production of biosurfactants was analyzed. We also studied bacterial features related to colonization inside the host plant, such as the type two secretion system (TTSS) and the expression of antioxidant enzymes.

The results obtained revealed that the white light decreases the bacterial growth with respect to blue light and darkness. It was observed that white light inhibits swimming and twitching motility. Regarding the production of biosurfactants, the strain presented the same emulsification capacity in all light conditions. However, the emulsification layer produced in sunflower oil by cultures grown under blue light exhibited a greater stability over time (about one month) compared with cultures grown under white light or darkness, indicating that, under blue light, the strain produces different biosurfactants than in the other light conditions. Finally, no differences were observed in the production of hydrolytic enzymes, but we have significant differences with respect to the expression of oxidative stress enzymes in white light, blue light and darkness. These results suggest that the *rsp0254* gene of Rso GMI1000 is functional and would be involved in the regulation of physiological features required for host plant colonization.

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P46-Correlation between photophysical properties and morphological changes of -Re(CO)$_3$(phen) pendants grafted to a poly-4-vinylpyridine backbone

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Photochemical and photophysical properties of a polymer, P4VP-Re(phen), consisting of ~200-[Re(CO)$_3$(phen)]$^+$ pendants grafted on a poly-4-vinylpyridine (P4VP) backbone, were interpreted on the basis of the morphological transformations. These Re(I) polymers, which are polyelectrolytes, exhibit interesting properties from a photochemical and nanoscience stand points[1-2].

In this work, we have used steady state and time resolved techniques to study the effect of nanoaggregation on the photophysical properties of P4VP-Re(phen). It was found that the P4VP-Re(phen) luminescence lifetime increases when the polymer concentration is increased (Figure 1). Also a nearly 8-fold increase in the luminiscence quantun yield resulted from the protonation of P4VP-Re(phen) with consequent changes of the excited state decay kinetics (Figure 2).

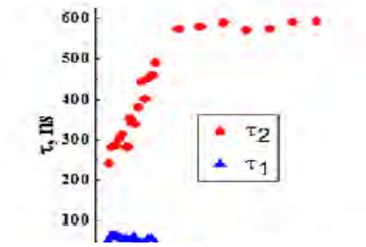
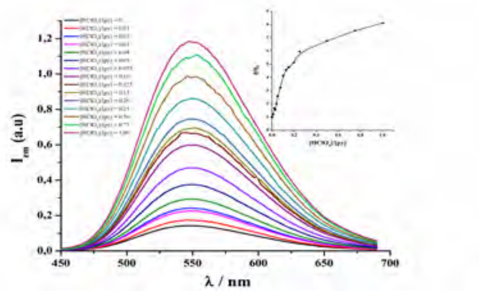


Figure 1: Dependence of the luminescence lifetimes, $\tau_{EM,}$ 1 and $\tau_{EM,}$ 2 on the concentration of P4VP-Re(phen).



Results of TEM and AFM morphological studies on P4VP and Re-P4VP in the presence of HClO$_4$ acid, i.e., to form Re-P4VPH$_n^{n+}$, revealed that they have concentration dependent morphologies (Figure 3).

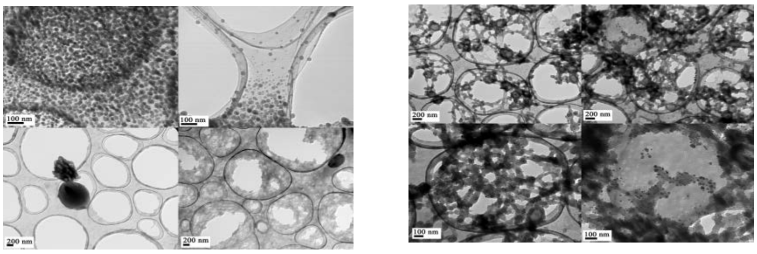


Figure 3: TEM images for: **a.** P4VP- Re(phen) polymer films, **b.** P4VP-Re(phen)H$_n^{n+}$ polymer protonated.

From low to large concentrations of the Re(I) polymer, the morphology of P4VP-Re(phen) varies from a nonhomogeneous distribution of spherical nanoaggregates coexisting with micrometer size fibres to an homogeneous distribution of spherical nanoagregates. The P4VP-Re(phen) morphology is also altered when the polymer pyridines are protonated.

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P47-Synthesis and Properties of Carbon Nanodots Obtained from Glucose and Urea by Microwave-Assisted Hydrothermal Carbonization

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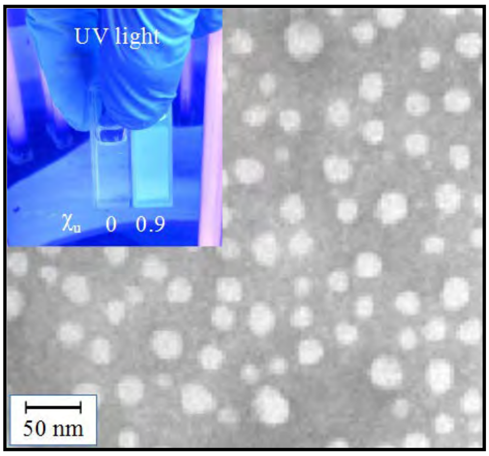
Carbon nanodots (C-dots) comprise discrete, quasiespherical nanoparticles with sizes bellow 10 nm. Recently, great advances had been achieved on the application of C-dots as luminescent probes for biosensing, bioimaging, drug delivery and optoelectronic devices [1]. C-dots can be prepared from numerous simple organic precursors and renewable natural products through economical, user-friendly and large-scale processes [2]. However, there is still debate about the functional groups, structure, and morphology of these particles whose variations determine their fundamental properties. The understanding of the correlation between these factors is further complicated by the strong dependence of C-dots properties with the nature of precursor materials and synthesis methods.

In the present work we explore a facile C-dots synthesis method based on hydrothermal carbonization of glucose *via* microwave pyrolisis. First, a glucose aqueous solution is mixed with a small amount of concentrated sulfuric acid and heated in a commercial microwave oven. The product (from yellow to dark brown solution to black residues, depending on power and reaction time) is then diluted/suspended in water, sonicated, and the C-dots extracted using 1-butanol as extraction solvent. After separation of the organic phase, the solvent is vacuum-evaporated and the particles resuspended in water and 0.45µm-filtered. Different reaction conditions, including variations in power, reaction time and concentrations of glucose and acid were tested. The incorporation of urea as a N-rich additive in the reaction mixture was also evaluated and the photophysical properties of the obtained nanoparticles studied as a function of the molar fraction of urea ($\chi_u = n_{urea} / (n_{urea} + n_{Glu})$). The nanoparticles were characterized by TEM, ATR-FTIR, UV-visible absorption, steady-state and time-resolved fluorescence spectroscopies, including determination of photoluminescence quantum yields (Φ_{PL}), and laser flash photolysis (LFP).



Quasiespherical C-dots with sizes bellow 25 nm were obtained in all cases. They form stable aqueous suspensions showing photoluminescence in the blue-green region with an excitation wavelength dependent behavior, and decays in the order of ns. In the absence of urea ($\chi_u = 0$), FTIR evidenced the presence of carbon doble bonds, carbonyl, carboxyl, alcohol and ether groups, while $\Phi_{PL} \sim 1\%$ was obtained, independent of the excitation wavelength (320-380 nm) and synthesis conditions. Including urea, and before $\chi_u = 0.7$, Φ_{PL} shows a maximum of about 2% at $\chi_u = 0.2$, with no significant changes on excitation-emission matrices. However, after $\chi_u = 0.7$, a large increase in Φ_{PL} was observed, peaking in $\chi_u = 0.9$ with $\Phi_{PL} \sim 10\%$, showing hypsochromic shifts both on excitation and emission spectra. For $\chi_u = 0$, a broad transient absorption spectrum, decaying in the µs time scale with maximum around 500 nm, appears both in the presence of molecular oxygen and after degassing with argon, while similar but less intense results were obtained for $\chi_u = 0.9$. The origin of the complex photophysical behavior of the C-dots obtained on increasing the urea content in the reaction mixture will be analyzed and discussed.

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P48-Excitation Energy Transfer and Trapping in Dye-Loaded Materials: Modeling and Numerical Simulations of Concentration Self-Quenching

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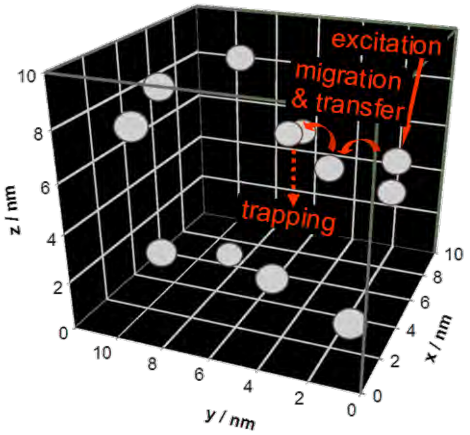
Dye-loaded materials, such as thin films or bulk solids, have potential applications in photosensitization, photocatalysis, solar cells and fluorescence labelling. In order to maximize light absorption, high concentrations of dyes are desirable. However, at high concentrations the formation of molecular aggregates and statistical traps generally dissipate the excitation energy, lowering the excited states population. The design of highly absorbing systems, avoiding energy dissipation, requires the knowledge of the photophysical parameters governing concentration self-quenching. For that reason, modeling of excitation energy transfer and trapping processes in dye-loaded materials is mandatory to identify critical design parameters to avoid energy dissipation and to reach maximum efficiencies. As an attemp to describe the photophysical processes in highly concentrated dyed materials, in the present work some modeling strategies of concentration self-quenching, including theoretical calculations and numerical simulations of excitation energy transfer and trapping, are presented.



As a first approximation, random distribution of dye molecules in two (2D) and three dimensions (3D) were considered. In the case of dyes with low aggregation tendency, Poisson statistics was used to asses the concentration of trapping centers, consistent in two or more dye molecules within a quenching radius, that show low interactions in the ground state but interact strongly in the excited state, leading to dissipation of the excitation energy. For 3D systems, theoretical calculations of energy migration and trapping rates, considering perfect, non-emitting traps, were performed using Loring, Andersen and Fayer (LAF) theory formalisms [1,2]. On the other hand, a Markovian matricial model was developed and numerical simulations of energy transfer and trapping were performed in 2D and 3D systems. While LAF theory is applicable for 3D random distributions of dye monomers and perfect traps, the Markovian matricial model allows numerical simulations of different dye distributions and system geometries and dimensionalities. However, depending on the complexity of the system considered, numerical simulations have a considerable computational cost. The comparison between LAF theory approach and numerical simulation predictions of concentration self-quenching will be presented, together with examples of the application of these models in the study of self-quenching in dyed materials [3-5]. Modeling aspects in the case of imperfect (emitting) traps will be also considered.

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P49-Photocatalytic degradation of catechol and caffeic acid using doped and undoped TiO_2 synthetized by sol-gel method

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The photocatalytic degradation of two phenolic compounds, catechol (CC) and caffeic acid (CA), was performed using TiO_2 and 0,1%Cu-TiO_2 (% = atomic percent) in a solution containing 50 and 25 [mg/L] of CC and CA respectively. TiO_2 and 0,1%Cu-TiO_2 were synthetized by sol-gel method. For CC, the experiments were carried out using a rectangular reactor with three UV lamps (365 [nm]) of 18 [W] each. For CA, the experiments were carried out using a different rectangular reactor under solar irradiation. During the experiments, the concentration of phenolic compounds was determined by UV-Vis spectroscopy by measuring the remnant absorbance at 275 and 312 [nm] for CC and CA respectively.

Both compounds have a certain degree of adsorption on the catalyst, which change color upon contact with the solution. As the experiment progresses and degrade pollutants, catalysts begin to restore its original color. For this reason, it can be determined that the photodegradation process is governed by a synergic mechanism in which adsorption and photodegradation are involved. Complete degradation of CC and CA was obtained at 300 and 150 minutes respectively. Total organic carbon and chemical oxygen demand analysis indicate that in these times has not yet reached complete mineralization of organic compounds. The total mineralization of all the intermediates present in the degradation of CC and CA was obtained at 480 and 210 minutes respectively. During the experiments, the pH of the solution drops to 4 in both cases, which begins to increase after mineralization. Degradation of organic compounds follows a kinetic pseudo-first order..

Acknowledgments: The authors thank the DGIP- UTFSM for their support through the Project Nº. 23.15.52.

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P50-Photophysical characterisation of Tröger´s base derivatives

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The interest in Tröger´s base analogues (TBs) emerged because the two aromatic rings fused to the central bicyclic framework are nearly perpendicular to each other, creating a rigid, V-shaped molecular scaffold with a distance of ca. 1 nm between the two extremities (Figure 1). In addition, TBs are chiral and fluorescent amines. Their chirality results from the very high energy barrier for the inversion of the nitrogen atoms and the fluorescence from the rigidity of the molecules. Due to these unique characteristics, Tröger's base derivates have countless potential applications, such as molecular recognition, catalysis, supramolecular chemistry and new materials among others [1].

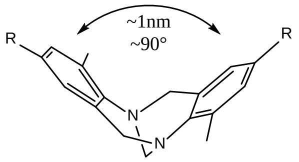
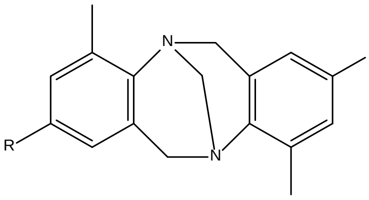


Figure 1



-R
1 -NC
2 -NH_2
3 -Br
4 -NHCHO

Figure 2

In the present work, four Tröger's base derivatives **1**–**4** (Figure 2) were synthetised in one to four steps, and their structures were confirmed by 1D and 2D NMR spectroscopy and mass spectrometry. Their stationary and dynamic photophysical properties were studied in hexane, dichloromethane (DCM), acetonitrile (MeCN) and ethanol (EtOH).

UV-Vis absorption spectra show bands centered in the 250–350 nm region for all compounds in every solvent, with high absorption coeficients of around 10^3–10^5 $M^{-1}cm^{-1}$, which are consistent with spin and simmetry allowed $\pi\pi^*$ transitions. All compounds emit in the 260–500 nm region and differences in the position and shape of the emission bands are observed, being strongly dependent both on the substituent and the solvent. These differences are most significant in DCM (Figure 3). The fluorescence decay profiles in hexane and EtOH show a biexponential time decay with lifetimes of approx. 1–2 ns and 5–7 ns. These results differ from those obtained in MeCN and DCM, where the decay profiles showed mono or biexponential behaviors depending on the substituent. In all cases, fluorescence lifetimes are consistent with $\pi\pi^*$ transitions.

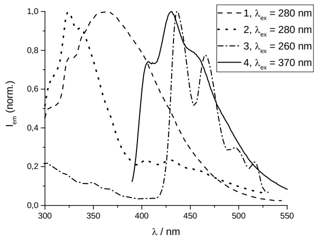


Figure 3

The largest solvatochromism is observed in **1** (Figure 4). This bathochromic effect indicates that the dipole moment is significantly larger in the excited state than in the ground state, which could be related to the extention of the aromatic conjugation to the isonitrile moiety. Specific solvent effects (i.e. hydrogen bonding) were observed for ethanol from the Lippert plot, whereas this behavior was not evident in other compounds.

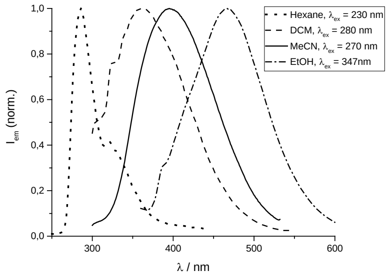


Figure 4

As a continuation of this work, time-resolved emission spectroscopy will be performed to analyze the photophysical reaction mechanisms and the excited state decays involved. Despite Tröger's bases interesting geometrical properties, almost no information regarding the photophysics and electronic structure of these analogues was reported [2] and this study represents one of the first approaches in this area.

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P51-Photophysical and photochemical study of new porphyrin dendrimers

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Porphyrin-based dendrimers (Pf-D) are compounds of interest, because they merge the recognized optical properties of porphyrins with the versatility of dendritic architecture in an unique class of macromolecules. Such features make these molecules especially suitable for light harvesting, photodynamic therapy (PDT) and photodynamic inactivation (PDI), which are topics of particular significance. Since PDT and PDI are driven by reactive oxygen species (ROS) generated by either energy or electron transfer from a sensitizer in an excited-state, the knowledge of the processes occurring after light absorption is essential to aim for the applicability of the Pf-D to human diseases. However, studies concerning the basis of the photophysical and photochemical properties of Pf-D are scarce and to the best of our knowledge there is no information in the bibliography about the characterization and dynamics of the triplet-excited states of Pf-D. Nevertheless, this topic is relevant as singlet oxygen ($^1O_2$) generation (the main ROS in PDT) is mediated by energy transfer from triplet-excited states of most sensitizers. It is known that porphyrins are chromophores yielding triplets with high performance and this is the main reason of its efficacy as PDT sensitizers.

Recently, Herández Ramírez and co-workers have synthesized a series of Pf-D based on meso-substituted tetra-(p-methoxy)phenyl porphyrins with PAMAM branches, and one peripherally-modified derivative with thiazole groups [1-2]. We are now interested in assessing the PDT/PDI capabilities of such Pf-D from *in vitro* characterization, with special enphasys on triplet-excited state properties and $^1O_2$ generation. In this work, we carried out a complete study on the photophysics and photochemistry of this Pf-D in dimethylformamide solution, by several spectroscopic techniques. Ground and singlet-excited states were characterized by absorption and fluorescence spectroscopies, respectively. Single photon counting was performed to obtain the singlet-state lifetimes. The triplet-excited states of the molecules were analyzed by means of laser flash photolysis, which allowed assessing the spectral and kinetic features of transient species formed after light absorption. Quantum yields of triplet generation (Φ_T) were estimated. Capability of the Pf-D as sensitizers of $^1O_2$ was evaluated by time-resolved phosphorescence of this species and the corresponding quantum yields (Φ_Δ) were calculated. Our results shows Φ_T and Φ_Δ in the order of those reported for Zn-tetraphenylporphyrin (ZnTPP), which was used as standard. It is important to note that the Φ_Δ obtained here are comparable to those reported for analogous porphyrin-based compounds, which have proven high efficacy in PDI of *C. albicans* cells [3]. Therefore, from these photo-physicochemical experiments we conclude that Pf-D might be used as efficient sensitizers in PDT and PDI applications.

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P52- Novel donor/acceptor setup for dye sensitized solar cells based on an aliphatic bridge. Computational design and experimental essay.

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Dye sensitized solar cells (DSSCs) are usually based on a rod molecule connected to a semiconductor or nanoparticle. The rod organic dye bears a donor (D) and an acceptor (A) moieties connected through a conjugated p system bridge (D-p-A).[1] Upon photoexcitation, the charge separation drawn in the lowest singlet (S_1) state (or in the relaxed S_1* state) is harnessed to store electrons into the semiconductor. An efficient charge separation in the S_1 state is the first requirement for a working DSSC, appart from many other factors which could enhace or deplete the efficiency, the fast charge recombination (back electron transfer) being one of the most relevant. Recently,[2] a Tröger base bridge (hereafter -s$_T$-), a strained heterocycle, has been proposed as an efficient but also selective bridge, capable of mediating the charge separation. Thus the setup D -s$_T$- A is here tested as a viable DSSC model dye, with the hope of taking advantages of its unusual charge separation properties.[2] In the present study the absorption and emission spectra of a pool of known 'conventional' dyads (D-p-A) were calculated using time-dependent DFT (TDDFT) approaches in order to find the best functional and solvation model for further prediction of novel (D -s$_T$- A) dyads.

Figure 1. Structures and transition densities for vertical S_1 state of **1a**

From the pool of novel dyads (D -s$_T$- A), four of the simplest ones are picked for detailed analyses. The evaluation was focused on the absorption wavelenght, on the existance of a lowest singlet with the maximum charge separation character (CT states) which would be able to be experimentally characterized by its fluorescence and on the appropriate redox potentials at the donor and acceptor edges. Compound **1a** (Figure. 1) is the simplest synthetic model and corresponds to the smaller D/A redox gap. Its parent **1b** lacks of the main donor group and could be taken as control. The absoprtion and emission spectra were simulated in solvents of increasing polarity from cyclohexane to acetonitrile and experimentally measured in the case of **1a/b**, they showing a good agreement between the experimental and calculated Stokes' shifts. From both the analysis of the experimental shifts and the calculated electron densities, the S_1 dipole moment was found to correspond to a CT state. However, the differences between **1a** and **1b** were rather mild, which indicates that the nitrogen of the bridge is the main donor of the systems and thus, although clear (Dm of 12 Debyes) the charge is not completely separated from on edge to the other. Relying on the good agreement between the energies and properties of the calculated excited states and the photophysical experimental data, several structures, **2a** among them, were proposed and they are currently being synthetized. By increasing the D/A gap, **2a** showed more than twice the dipole change observed in the **1a** parent (or in its own control **2b**). On the other hand, the analysis of the transition densities indicates that the charge is completely separated in the emitting state, in contrast to the partial separation shown on Fig. 1for **1a**. Based on the the properties of the relaxed S_1* state of **2a**, a set of other dyads were envisaged with a complete charge separation on their emitting states and at different absorption and emission wavelenghts, which could be considered as proof of principles models for these novel DSSCs.

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P53- Corticoids Photodegradation in Homogenous and Micro-heterogeneous Media. Cytotoxicity of Photoproducts

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The use of biologically active substances with anti-inflammatory properties such as corticosteroids has increased considerably in the last decades. Particularly, the compounds of our interest: Prednisolone (Predn), Prednisone (Pred) and Dexamethasone (Dx) belong to the family of glucocorticoids (GC) most commonly used.

Two aspects related to the interaction of the pharmaceuticals with light are of great interest. On the one hand the photostability of these compounds during their production and storage, and on the other hand their photodecomposition in less aggressive species to the environment when the drugs are removed, metabolized or not, throughout effluents. These GC absorb UV-B radiation and may participate in photochemical processes, which can result in their own decomposition by unimolecular photodegradation or by the attack of reactive oxygen species (ROS) generated from the interaction of the GCs excited states with oxygen.

In these sense, kinetic and mechanistic aspects of the direct photodegradation of GCs have been studied in aqueous and micro-heterogeneous medium under different atmospheric conditions by stationary and time-resolved techniques. Also, the cytotoxicity of the GCs and the photoproducts generated in different atmospheres were evaluated on model cell lines.

P54-Effect of Cholesterol Content 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 [1]. 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 it remains unclear how the lipid content and the lipid phase packing order of membranes could be involved [2-3].

In this study, the effect of cholesterol on the activity of ISAv fusion peptides was analyzed. The ISAv 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 adopts a mainly helical conformation. The partition constant (Kp) of the peptides was obtained using the tryptophan steady state fluorescence anisotropy technique present in the peptides.

In addition, we evaluated the effect of the cholesterol content on the phospholipid acyl chain packing order of vesicles. In this case, we studied the fluorescence anisotropy of DPH derivatives on the proposed lipids mixtures. On the other hand, the kinetics of fusion pore formation were studied through terbium/dipicolinic acid (Tb/DPA) fluorescence enhancement assay and hemifusion by fluorescence resonance energy transfer (FRET) using N-(7-nitrobenz-2-oxa-1,3-diazol-4-yl)-1,2-di-hexadecanoyl-sn-glycero-3phospho-ethanolamine (N-NBD-PE) and lissamine rhodamine B-1,2-dihexadecanoyl-sn-glycero-3-phosphanolamine (N-Rh-PE). Our results showed that the cholesterol content of the vesicles affects the fusion of the membranes mediated by ISAv fusion peptides.

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P55- Photosensitized membrane damage by lipophilic pterin derivatives

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Lipid peroxidation processes are thought to be involved in a number of physiological and pathological events and arise by different mechanisms, such as free radical, enzymatic and photosensitized reactions [1]. Pterins are heterocyclic compounds widespread in nature and have been previously identified as good photosensitizers under UVA irradiation [2,3]. It is known that pterin (Ptr, Figure 1), the parent compound of oxidized pterins, is able to freely cross the phospholipid bilayer but, nevertheless, produces photosensitized membrane damage in large unilamellar vesicles (LUVs) [4]. Therefore new lipophilic pterins (pterins **1** and **2**, Figure 1) have been synthesized. Their structure allow them to intercalate in lipid biomembrane with high binding constants. In addition, they absorb in the UVA region and are able to generate singlet oxygen by photosensitization. Moreover, pterin **2** is more photostable than pterin **1** under UVA irradiation [5].
The aim of this work was to investigate the damage to lipid membranes by the lipophilic pterins upon UVA irradiation. Comparision with Ptr were made. LUVs of soybean phosphatidylcholine (SoyPC LUVs) were used as model membrane. LUVs containing a photosensitizer were irradiated with UVA light and different analyses were performed. Conjugated dienes and trienes were determined by absorption at 234 and 270 nm respectively. Peroxidation of SoyPC resulted in an important increase in the rate of conjugated dienes production when using pterins **1** and **2** comparing to Ptr. Other experiments were performed to evaluate the production of hydroperoxides, such as FOX2 assay. Furthermore, giant unilamellar vesicles (GUVs) were used to detect the increase of permeability of the membrane by a photosensitized damage.
As a conclusion, UVA irradiation of pterins **1** or **2** with SoyPC LUVs led to the lipid peroxidation of polyunsaturated fatty acids generating mainly hydroperoxides. A higher rate of peroxidation was detected when comparing to Ptr as photosensitizer. Membrane permeability is rapidly increase when using pterins **1** and **2** as photosensitizers on GUVs.
Therefore, these new lipophilic pterins are more effective to use as photosensitizers in membrane models then Ptr itself and could be further use in different processes, such as photodynamic inactivation.

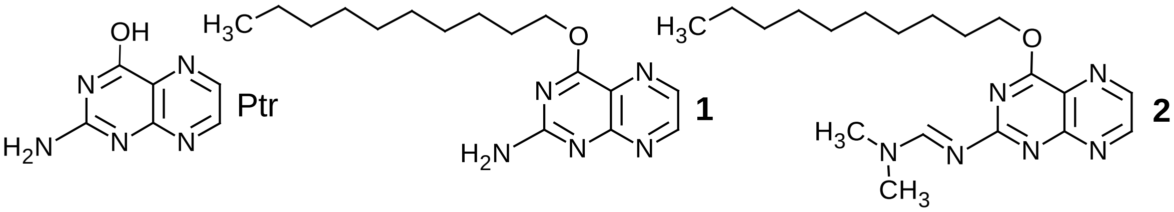

Figure 1. Chemical structures of Ptr and lipophilic pterins.

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P56- Evaluation of the potential antioxidant and antimicrobial capacity of the phenolic compound 2-(2-hydroxyethyl)-phenol in the presence of Riboflavin.

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Food and beverages are exposed to UV and visible light during their processing, storage and consumption. Both UV and visible light are capable to affect food quality, modifying the chemical structure of the components through oxidation reactions. These reactions cause loss of nutrients and bioactive compound, the formation of undesirable odors and flavors and the formation of potentially toxic substances. Riboflavin (Rf) or vitamin B2, is a water-soluble vitamin, present in many foods, mainly dairy products and beverages. Its interaction with light is often the cause for degradation of these products as result of a process of photosensitization. This vitamin can act as a photosensitizer through a singlet oxygen O_2 ($^1\Delta_g$) pathway (Type II) and / or by free radicals (Type I). Although O_2 ($^1\Delta_g$) is one of the most common reactive oxygen species (ROS), the superoxide anion radical ($O_2^{-\bullet}$), hydroxyl radical ($HO^{\bullet}$) and hydrogen peroxide (H_2O_2), can also be generated through Type I pathway, therefore, such species are also important in many of the photosensitized processes. For this reason, the preservation of fatty products to the ROS effect is a point of capital importance. Industries try to avoid fatty products oxidation by the addition of antioxidants. Antioxidants may be defined as substances that, when present in food, delay, control or inhibit the oxidation and deterioration of food quality [1]. In particular, phenols are non-enzymatic scavengers of ROS and free radicals. They are considered as primary antioxidants or lipid oxidative chain breakers, since they deactivate ROS in their initial stages and prevent oxidative process continues [2-3].

The aim of the present work was the study of the potential interaction of 2- (2-hydroxyethyl) phenol (2-OH) with photo-generated ROS through the sensitizing action of Rf. A kinetic-mechanistic study was carried out to evaluate the 2-OH photo-stability against different photo-generated ROS and microbiological assays to evaluate the antimicrobial capacity of this substrate against *Escherichia coli*.

Results demonstrate the existence of interactions between the 2-OH substrate and ROS. The species O_2 ($^1\Delta_g$), $HO^{\bullet}$ and H_2O_2 are involved in the photodegradation process of 2-OH, sensitized by Rf. In addition, the studies show that 2-OH, interacts with excited singlet state and excited triplet state of Rf. In presence of commercial antioxidants, such as Trolox and ascorbic acid, 2-OH substrate shows a synergistic effect with them. *In vitro* studies show the system Rf/2-OH has antimicrobial activity against *E. coli* under assayed conditions.

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P57- Comparative study of the photodegradation of Triclosan, an emerging contaminant, by Photo-Fenton in homogeneous and micro-heterogeneous medium.

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Emerging contaminants (EC) are define as unknown or unrecognized contaminants whose presence in the environment is not necessarily new but the possible consequences that they can have in the ecosystem are being widely studied and detected. They´ve been found to have the potential to produce an ecological impact as well as adverse health effects [1].

In the present work, 5-chloro-2- (2,4-dichlorophenoxy) phenol, commonly known as Triclosan (TCS) [2], was chosen as EC. TCS is a broad-spectrum fungicide and antimicrobial and it reaches the environment usually through wastewater and has a negative impact on aquatic ecosystems due to its persistence in natural waters, causing potential long-term risks to human health [3].

The Fenton and Photo-Fenton processes are characterized by generating the species $HO^{\bullet}$, which is a highly reactive ROS and often causes the mineralization of organic compounds. Traditionally, these systems are studied in aqueous media due to the high reactivity of $HO^{\bullet}$ with organic solvents, therefore its study and application has been centered on water-soluble compounds.

Given the low solubility of TCS in aqueous media, it was decided to work with a cyclic oligosaccharide, β-Cyclodextrin (β-CD), formed by 7 molecules of glucose that constitute a cavity of 6-6.5 A in diameter, joined by α-1,4-glycosidic bonds. This cavity can receive another molecule (host) as long as it has the correct size and shape [4]. The low toxicity and cost, in addition to the intrinsic properties of CDs, leads to their use for increasing solubility, stability and bioavailability of different substances [5]. In the particular case of TCS, the association constant of the TDS-β-CD complex was determined by UV-Vis spectrophotometry using the Scott equation [6], obtaining a value of 6754 M^{-1}. This system was computationally simulated using Gaussian 09.

In order to evaluate the photodegradation of the EC, a study of the Photo-Fenton reaction was carried out in homogeneous (without β-CD) and micro-heterogeneous media (with β-CD). To perform the photolysis experiments a Rayonet reactor equipped with eight 8 W lamps, whose emission is centered at 365 nm, was used and the degradation of the TCS was monitored by HPLC-UV following the λ_{max} of the compound (280 nm). It was found that the degradation ratio of TCS in homogeneous medium (TCS solution in H2O with 10% of ACN), after 4hr of irradiation reach a 93% conversion whereas for the same conditions of irradiation in micro-heterogenous medium (TCS solution in H2O and β-CD) is only 48%. This can be attributed to the formation of the TCS-β-CD complex, which decreases the availability of TCS for its photodegradation [7], preventing its reaction with HO.

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P58- Effect of different light sources on phenol degradation using a metal-doped TiO_2 catalyst

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Conventional methods of treating industrial effluents can not effectively remove refractory contaminants, such as phenols. An alternative treatment is the use of advanced oxidation processes. Many of them are based on the use of TiO_2 as a photocatalyst [1]. However, the use of TiO_2 has several limitations. It has been found that the modification of this material with metals (noble, transition or lanthanide) shown an enormous potential to overcome the pristine TiO_2 particles limitations of visible light absorption and high recombination of charge carriers [2,3]. The aim of this work is to study the effect of different light sources on phenol degradation (model contaminant) using metal-doped TiO_2 catalysts (metal: V, Pd or Ce, 0.1 at.%).

The materials were prepared by the sol-gel method. The procedure was described in a previous paper [4].The specific reagents used in this synthesis were: titanium tetraisopropoxide (TTIP), absolute ethanol, nitric acid and, cerium(III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$), palladium acetylacetonate ($Pd(acac)_2$) or vanadyl acetylacetonate ($VO(acac)_2$) as metal-ion precursor.

X-ray diffraction analysis exhibited only anatase phase in all samples, with crystallite size between 6.8 and 10.1 nm (estimated by Scherrer equation). The BET surface area values were between 80 and 110 m^2g^{-1} (N_2 physisorption). The diffuse reflectance spectra of metal-doped TiO_2 catalysts showed a band broadening to the visible region over the range of 400-800 nm, with E_{GAP} values between 1.9 and 2.3 eV.

Degradation of phenol in aqueous solution ($[phenol]_0$= 50 μM) was studied with irradiation of different light sources (Rayonet RPR-100 with UV or visible lamps) and 1 gL^{-1} of each catalyst. In all cases, periodic sampling was carried out. The concentration of phenol and reaction intermediates were determined by HPLC (HP 1050).

The Figure 1 shows the percentage of phenol degradation with each catalyst after 3 or 5 hours under UV or visible irradiation, respectively. All the materials presented photoactivity while the efficiency with UV lamps was higher than with visible lamps. It is noteworthy that 0.1Pd catalyst reached total degradation with UV lamps after 2 hours of irradiation.

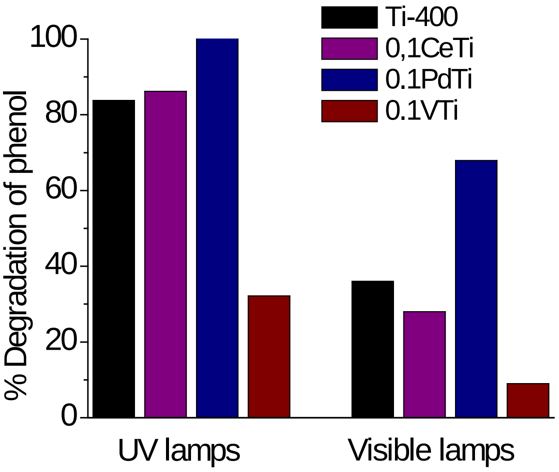

Figure 1: Effect of different light sources on phenol degradation.

Acknowledgments: The authors would especially like to thank P. Fetsis for his experimental contribution to adsorption-desorption isotherms of N_2 measurements.

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P59-Absorption of ADPA on the surface of conjugated polymer nanoparticles and its effect in the determination of $\Phi\Delta$

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The determination of singlet oxygen $O_2(^1\Delta_g)$ quantum yields (Φ_Δ) is of great importance when characterizing new photosensitizers for photodynamic cancer therapy (PDT) [1,2], water photodecontamination [3], etc. There are direct and indirect methods for the determination of Φ_Δ. Direct methods estimate Φ_Δ by quantifying the characteristic $O_2(^1\Delta_g)$ phosphorescence in the NIR region (1270 nm). Indirect methods are based on the evaluation of the rate of oxidation of $O_2(^1\Delta_g)$ chemical traps. Among the most commonly used traps are dimethylanthracene (DMA) and its hydrophilic derivative, i.e. sodium 3,3- (anthracene-9,10-diyl) dipropionate (ADPA). These traps have characteristic absorption bands at ~ 400 nm and react efficiently with $O_2(^1\Delta_g)$ to form the corresponding endoperoxides, which are transparent at that wavelenght. Thus, the $O_2(^1\Delta_g)$ production kinetics and consumption can be easily monitored by UV-vis spectroscopy [4].

We report herein on the syntesis of nanoparticles (NP) of poly (9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) undoped and doped with platinum octaethylporphyrin (PtOEP) and their capacity for generating $O_2(^1\Delta_g)$. NPs were characterized by UV-vis absorption and stationary and time-resolved emission spectroscopies. The morphological characterization was carried-out by atomic force miscroscopy (AFM). Φ_Δ were determined by direct and indirect method using eosin-Y as reference. Results obtained from $O_2(^1\Delta_g)$ phosphorescence measurements show that NPs doped with 10% w / w PtOEP have a $\Phi_\Delta = 0.24$, which is ~3 times greater than that of undoped F8BT NPs, i.e. $\Phi_\Delta = 0.09$. However, Φ_Δ obtained from the indirect method, *ca.* from the oxidation rates of ADPA, are substantially higher, *i.e.* 0.69 and 0.22 for the doped and undoped NPs, respectively. The discrepancy between the results obtained by the methods motivated us to carry-out a more detailed study of the oxidation processes of ADPA sensitized by the F8BT NPs. From these studies it was concluded that the indirect method overestimates the valores values due to the ADPA adsorption on the NPs surface. The concentration of ADPA adsorbed on the NPs was estimated by comparing the NPs excitation spectra in absence and presence of different concentrations of ADPA. Applying the Langmuir adsorption model, the number of bond sites per particle (~14000) and the equilibrium constant associated to the adsorption process (~ 8000 M^{-1}) were determined. Since $O_2(^1\Delta_g)$ is generated on the NP surface where a fraction of ADPA resides, the oxidation efficiency of the chemichal trap increases significantly, resulting in overestimated Φ_Δ values. These results caution about the use of ADPA as a probe to evaluate Φ_Δ in these systems.

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P60- Photoinduced color change of natural dyhydroxyanthraquinones solutions isolated from *Heterophyllaes lycioides*

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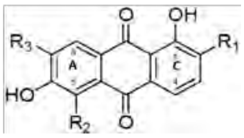
Chemical study of *H. lycioides* allowed the isolation of seven anthraquinones, three of them reported as novel for this family of compounds [1]. It was demonstrated that five of them: soranjidiol (Sor), 5-chlorosoranjidiol (5-ClSor), bisoranjidiol (Bisor), lycionine (Lyc) and 7-chlorobisoranjidiol (7-ClBisor) (Fig. 1) are potencial photosensitizers compounds to be applied in Photodynamic Therapy (PDT) [1,2]. Nevertheless, photoinduced color changes (either by degradation or molecular rearrangements) of photosensitizer solutions is one of the critical requirements necessary for efficent PDT. Hence, in this report we compare the UV-Vis spectral changes of the following natural monomeric and dimeric dihydroxyanthraquinones compounts DHAQs:

a



DHAQs	R1	R2	R3
Sor	CH_3	H	H
5-ClSor[1]	CH_3	Cl	H
Bisor*	CH_3	Sor	H
7-ClBisor*[1]	CH_3	Sor	Cl
Lyc*[1]	CH_2OH	Sor	H

b

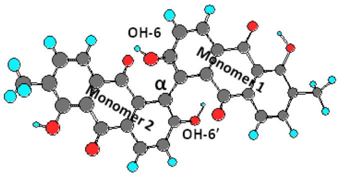


Fig. 1a. Soranjidiol derivatives. *bianthraquinones formed by two soranjidiol monomers linked in position 5-5´. [1]New anthraquinones isolated from *H. lycioides*. **b.** Three-dimensional structure of Bisor.

Steady state photolysis of DHAQs in air-saturated solutions of $CHCl_3$ were performed during 3 h using a 1 W Royal Blue LED (λ_{max}= 444 ± 27 nm) and the spectral changes were monitored *in situ* using an optical fiber-guided diode array spectrophotometer (Ocean Optics), collecting full spectral data between 220-800 nm every 1 min.

For the monomeric DHAQs Sor and 5-ClSor no changes in the UV-Vis spectra after 3 h of irradiation were observed, indicating that these compounds were highly photostable. Nevertheless, blue-ligth irradiation of dimeric DHAQs Bisor and 7-ClBisor produces a relatively rapid hypsochromic shift of the absorbance band, resulting in the progresive fade of the initial yellow color of the irradiated solutions. Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) analysis of UV-Vis spectra showed the presence of intermediate species during the formation of the final photoproduct, being the photoconvertion much faster for 7-ClBisor than for Bisor. However, after dark storage of the transparent irradiated solutions during few days, a yellowish color of the solution was recovered, suggesting that the photoinduced color fading is partially reversible. However, in the case of Lyc, the photoinduced hypsochromic shift was almost permanent even after 10 days post-irradiation and the MCR-ALS analysis did not showed the presence of intermediate species. This photochromic effect of the dimeric DHAQs could be explained as a result of photoinduced atropoisomerization in the triplet excited state due to the lower activation energy (<10 kJ/mol) barrier necessary for the physical rotation on the biaryl axis that characterizes these structures [3]. This rotation out of plane reduces the aromatic coupling between the two DHAQ moieties through the ring A of each monomer, modyfing the absorption spectrum and changing the color of AQs solution. The reversible color recovery under dark conditions is governed by a much larger energy barrier (>100 kJ/mol) depending of the molecule structure.

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P61- Solvent effects on the formation of Resveratrone

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Cosmeceuticals skin products and pills containing antioxidants are getting more popular every day. The enormous therapeutic potential of RSV in treatments of a wide variety of diseases have been postulated and/or demonstrated [1]. However, most of the adverse effects under UV radiation are unknown. Moreover, recent articles mencioned the generation of 4-(6,8-dihydroxynaphthalen-2-yl)but-3-en-2-one, known as resveratrone (RSVT), when *trans*-resveratrol (*t*-RSV) and/or *cis*-resveratrol (*c*-RSV) are exposed to UV radiation.

In this work, the photodegradation of *t*-RSV and *c*-RSV in aqueous and ethanol solutions were investigated employing high pressure liquid chromatography (HPLC) coupled to UV-spectrophotometry and mass spectrometry detectors. The solutions were irradiated with UVB and UVA for different irradiation times at 298 K.

Several products were identified, both in the presence and the absence of oxygen. One of the products obtained was the RSVT (Figure 1). Structure of molecule consists of two fused aromatic rings with two hidroxyl groups linked to a linear chain containing a carbonyl group. This novel compound was recently characterized, and it is highly fluorescent with a fluorescence quantum yield up to 0.5 in some solvents. This characteristic is being analyzed to be used as organic fluorophore in bio-imaging [2][3]. The phenantrene-like photoproducts can acts as photosensitizer producing singlet oxygen [4] promoting the oxidation of macromolecules.

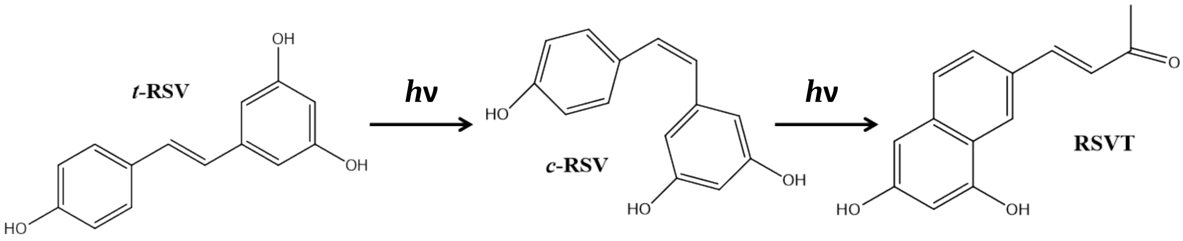

Figure 1: Formation route of RSVT

Acknowledgements
The present work was partially supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET-Grant PIP 112-200901-00425) and the Scientific cooperation program CONICET-CNRS (PICS No. 05920). M. G. T. thanks CONICET for post-doctoral research fellowships.

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P62- Photosensitised Degradation of Phenol by Visible Light and a Riboflavin-derivative adsorbed on the Surface of TiO_2

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Contamination of surface water due to poor agricultural practices and excessive use of pesticides is a growing problem in our country. Recently CASAFE (Chamber of Pesticides in Argentina) reported that the consumption of pesticides increased 858% in the last 22 years [1].

Among the alternatives for the treatment of toxic organic pollutants in the water or effluents, called advanced oxidation processes (POAs) are one of the most attractive, most of them are characterized by hydroxyl radicals ($OH^{\bullet}$) in quantity sufficient to oxidize most of the organic compounds. The treatment of water by heterogeneous photocatalysis using titanium dioxide as a catalyst is one of the most interesting POAs among the scientific community [2] since it is inert and highly chemically stable. However, photodegradation processes using TiO_2 requires light with wavelength less to 370 nm, which represents less than 5% of the solar radiation that reaches the earth. In this sense, the sensitization processes resulting from the photoexcitation of dye molecules (sensitizers) have succeeded in increasing the degradation efficiency of TiO_2 with sunlight. Photosensitization is a convenient method to extend the photoresist of semiconductor materials to the visible region. Typically, the dye is adsorbed on the surface of the semiconductor and absorbing visible light reaches excited state(s) which are capable of injecting electrons into the conducting band of the semiconductor.

This paper reports the characterization of films based on TiO_2 and Rf-PO_4 synthesized by two different methodologies. *Procedure 1:* The dye was adsorbed on the surface of TiO_2 by immersion of the film in a Rf-PO_4 solution after sintering the TiO_2 for 30 minutes at 500°C. *Procedure 2*: The dye was incorporated to the TiO_2 previously to the sintering process at 180ºC to prevent the Rf-PO_4 thermal degradation.

To test the photocatalytic efficiency of the developed system, phenol was chosen as the model pollutant. The discharge of phenolic compounds from industrial sources such as synthetic resins, petroleum refineries and coke oven processes, even at low concentrations, poses a major threat to aquatic organisms [3]. For the sensitized photodegradation process of phenol, a solution was irradiated in the presence of the different films synthesized. Also, different sources of radiation (simulated solar light and blue LEDs) were used for photodegradation. Comparative studies were carried out between the different films to evaluate the degradation efficiency of phenol.

Material used for photodegradation	% Degradation of phenol with 40 min of irradiation	
	Simulated solar	LEDs light
Procedure 1	10	10
Procedure 2	25	20
film of TiO_2 alone	5	0

Identification of the photoproducts was made by HPLC. In all cases, the majority photoproducts coincided with the products generated by Phenol photodegradation by a TiO_2 suspension [4].

In conclusion, the better degradation performance was obtained using the film synthesized by the procedure 2. In addition, the union of the Rf-PO_4 on the TiO_2 allowed extending the photoresponse of the film to the visible region, obtaining a greater efficiency for the degradation of the Phenol.

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P63-Photoinduced visible regeneration of NADH cofactor mediated by NH_2-MIL-125

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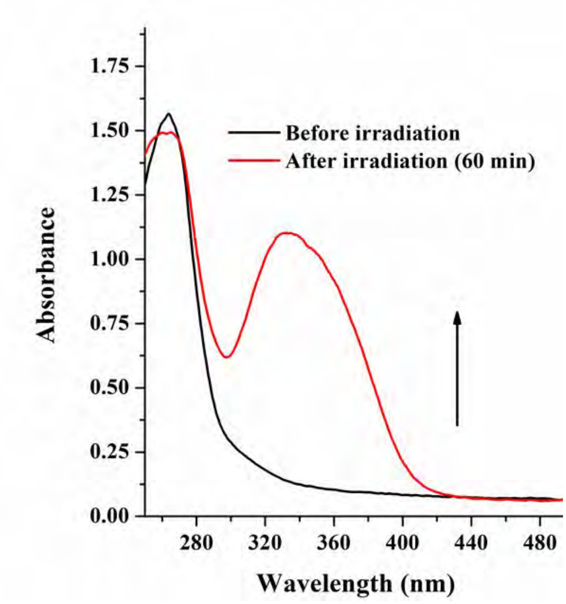
Enzymatic catalysis is an interesting approach to carry out chemical reactions with low energy cost and high specificity. However, its practical application requires the development of efective methods of immobilization to facilitate enzyme recovery and reuse. As part of our ongoing efforts in this line of research, we have recently used metal-organic frameworks (MOFs) to develop hybrid systems coupled with magnetic particles for the immobilization and recycling of formate dehydrogenase enzyme to mediate the reduction of carbon dioxide. Metal-organic frameworks are a class of hybrid materials made up from inorganic centres (metal ions or metal oxide clusters) coordinated by organic molecules. [1] These materials are very interesting because of their high surface areas and particularly because of their semiconductor properties, which can be exploited for the development of photobiocatalysts either to activate the enzyme directly or to regenerate the cofactor (*i.e.*, Nicotinamide Adenine Dinucleotide, NADH). It is noteworthy to recall that bibliographic reports of the regeneration of NADH often involve the photoexcitation of rare and expensive metal complexes such as ruthenium, plasmonics nanoparticles of Pt or semiconductors of toxic nature as CdS.[2]

In this presentation, we report the use of NH_2-MIL-125 as a photoactive species to mediate NADH regeneration induced by visible irradiation from its oxidized form (NAD^+). NH_2-MIL-125 is a metal-organic framework based on titanium oxo clusters and aminoterephthalic acid as ligands, which good biocompatibility, strong absorption response in the visible region ($\lambda_{onset} \approx 550$ nm) and efficient photoinduced charge separation. [3]

The regeneration of NADH was performed by visible irradiation ($\lambda_{irrad} \geq 400$ nm) under anaerobic conditions of aqueous suspensions of NH_2-MIL-125 in the presence of NAD^+ and isopropyl alcohol as a sacrificial electron donor. The evolution of NADH in the solution was evaluated by UV-Visible spectroscopy monitoring the absorbance at 340 nm (see Figure) and by emission spectroscopy. The synthesis and characterization of the photocatalytic material as well as the mechanism of NADH photo-regeneration is discussed in detail.



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P64- Effect of metal ions on the reactivity of flavonoids towards singlet oxygen

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Flavonoids are polyphenolic compounds widely present in fruits, vegetables and some processed products such as tea, wine and chocolate. They are recognized for their antioxidant capacity, in addition to their anti-inflammatory, anti-allergic, antiviral and protective role against heart diseases, cancer and different pathologies [1].

The antioxidant action of flavonoids has been extensively studied against different radical oxidant molecules. We recently showed that flavonoids are good quenchers of singlet oxygen [2] and could be valuable antioxidants against this reactive oxygen species in systems under oxidative stress.

Several mechanisms have been proposed to account for the antioxidant action of these, e.g., hydrogen abstraction, electron transfer and complexation with metal ions [3-5]. The complexation of flavonoids with metal ions inhibits the reactions in which these metals participate and generate radicals, such as the Fenton and Haber-Weiss reactions. However, it has also been proposed that the complex formed not only prevents oxidation due to the limitation of a reactant, but also increases its antioxidant capacity and modifies its biological action [6].

In a few studies related to the reactivity of flavonoids with singlet oxygen, has been observed that metal ions increase the reactivity of flavonoids and that this effect could be ascribed to the formation of an association complex between the flavonoid and the metal ion [7,8].

In this communication, we report the effect of metal ions Ca^{+2}, Cu^{+2} and Zn^{+2} on the reactivity of Quercetin, Morin and 3-hydroxyflavone towards $^1O_2$. Benesi-Hildebrand treatment shows the flavonoids forms 1:1 or 1:2 (metal:flavonoid) association complexes with Ca^{+2}, Cu^{+2} and Zn^{+2}. The association constants are in the order of 20-300 M^{-1} for Ca^{+2} and 20.000 M^{-1} for Cu^{+2} and Zn^{+2}, with methanol as solvent. In addition, in the presence of an excess of metal ion, the reactivity of these substrates towards singlet oxygen increases approximately by 1-2 orders of magnitude. A kinetic scheme accounting for this effect is proposed and discussed.

Acknowledgements. Financial support of research project FONDECYT 1150210 and CONICYT graduate fellowship N° 21151626, is gratefully acknowledged.

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P65- Photophysical Characterization of Mononuclear Re^I Complexes with Pyrazolyl-Pyridazine Ligands

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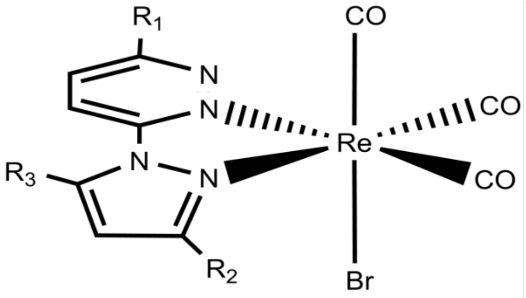
Rhenium(I) diimine tricarbonyl complexes have attracted the researchers attention during the last decades because of their useful photophysical properties, well-behaved synthesis and stability.[1] Simple imines like pyrazolyl-pyridazine derivatives are appealing candidates to be explored, owing to their planarity and limited conformational flexibility which diminishes non-radiative deactivation paths.[2]

In this work the photophysical behaviour of Re(I) complexes were studied in several solvents. These compounds present absorption bands in the UV and blue region with low molar extintion coefficients which can be ascribed to metal to ligand charge transfer (MLCT) transitions. Emission bands centered around 600 nm with low emission quantum yields and emission lifetimes ranging between 30 and 300 ns. No dependence on the solvent polarity was observed for their photophysical behaviour. In general, these complexes have moderate to higher quantum yields of singlet oxygen generation. Moreover, TEA addition results in a decrease of emission intensity with a Stern Volmer constants in the order of 10^4 M^{-1}.



I : R_1 = H R_2= H R_3 = H
II : R_1 = Cl R_2= H R_3 = H
III : R_1 = COOH R_2= CH_3 R_3 = CH_3
IV : R_1 = N-pyrazolyl R_2= H R_3 = H
V : R_1 = N-pyrazolyl R_2= H R_3 = CH_3

Chemical structures of Re(I) complex studied.

Acknowledgements: Authors acknowledge to grant Fondecyt 1160546, PIA Conicyt Anillo ACT 1404.

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P66- Photophysical Characterization of an Anthracene Analogous of Laurdan.

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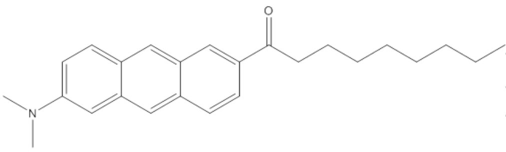
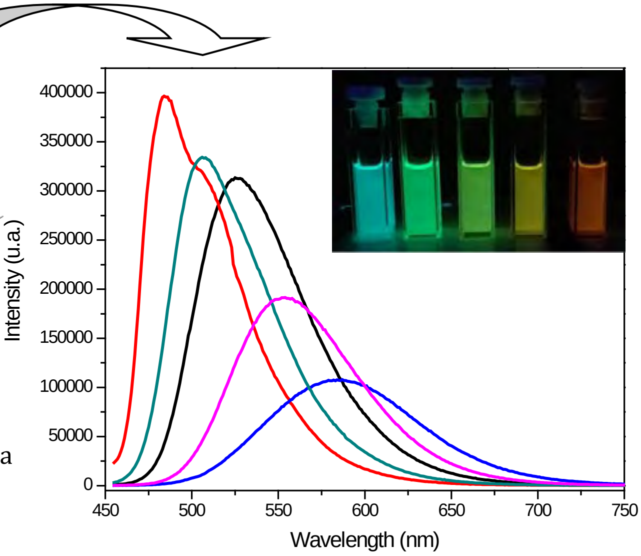
According Weber's definition, for an hydrophobic fluorescent probes to be used as an environmentally sensitive sensor, it must have in its structure two different substituents, having electron acceptor an donnor character respectivelly., both attached to an aromatic ring. The magnitude of the sensitive 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.

In order 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.[1]

The photophysical behaviour of Capyrdaa in homogeneous media shows an important 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.

According preliminar fluorescence microscopy determinations in microheterogeneous systems Caprydaa behaves as a good probe.





Chemical structure and emission of Caprydaa

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P67- Degradation of Ciproflaxacin and Lomefloxacin mediated by photogenerated ROS

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Ciprofloxacin (CPFX) and Lomefloxacin (LMFX) correspond to the family of fluoroquinolones compounds, a group of antibiotics which have been used for the treatment of several infectious diseases.

Some studies have reported the ability of CPFX and LMFX to generate Reactive Oxygen Species (ROS) after UVA radiation, producing phototoxicity in mice and in human cells [1]. Furthermore, it was observed that $^1O_2$ photogenerated under UVA irradiation of CPFX and LMFX, may cause DNA damage in human cells [2]. Likewise, other studies have demonstrated the role of oxidative stress induced by fluoroquinolones in bactericide activity of these compounds [3], [4].

Though some studies yield information about CPFX and LMFX ability to produce ROS, it will be of great interest to investigate the potential ROS-mediated degradation of both fluoroquinolones, which may be exposed at oxidative stress scenery.

In this contribution, photodegradation of CPFX and LMFX by ROS was studied through photosensitized processes. Riboflavin (RF) and Perinaphtenone (PN) were employed as the photosensitizers. Visible light irradiation of aerated aqueous solutions of CPFX and LMFX in presence of RF have shown spectral modifications, which may be interpreted as chemical degradation of both fluoroquinolones and the photosensitizer. In parallel, oxygen consumption by CPFX and LMFX was observed. The latter results suggest the potential interaction between the fluoroquinolones and the electronically excited states of RF and/or ROS generated upon photoexcitation of the pigment. CPFX and LMFX interact with the electronically excited triplet state of RF ($^3RF^*$) with rate constants (^3k_q) of 20.4 ± 0,2 x10^8 M^{-1}s^{-1} and 29.8 ± 0,3 x10^8 M^{-1}s^{-1}, respectively. Besides, oxygen consumption experiments in the the absence and in presence of specific ROS inhibitors (Sodium Azide for $^1O_2$, Superoxide Dismutase for $O_2^{\bullet -}$, Catalase for H_2O_2 and Benzoic acid for Hydroxyl radical) suggest the participation of $^1O_2$, $O_2^{\bullet -}$, H_2O_2 and $OH^{\bullet}$ in Rf-photosensitized CPFX and LMFX photodegradation.

In order to quantify the $^1O_2$ participation in both fluoroquinolones photodegradation, studies using PN were performed. Both, overall and reactive interactions between $^1O_2$ and CPFX and LMFX were quantified through the rate constants k_t and k_r, respectively. k_t values were 48.7 ± 0,5 x10^7 M^{-1}s^{-1} for CPFX and 93.7 ± 0,9 x10^7 M^{-1}s^{-1}for LMFX, while k_r values were 1.61 ± 0,2 x10^7 M^{-1}s^{-1} for CPFX and 5,4 ±0,5 x10^7 M^{-1}s^{-1} for LMFX.

As can be seen, these results suggest that under RF-sensitized photodegradation, both antibiotics may interact with $^3RF^*$. This result points to the potential degradation of CPFX and LMFX under oxidative stress conditions. From k_t values, it seems that LMFX is a better $^1O_2$ quencher than CPFX. From k_r/k_t ratios, it can be noticed that the reactive contribution to the overall deactivation of $^1O_2$ by both compounds represent around 5%. Therefore, around 95 % of $^1O_2$ deactivation by both antibiotics is due to physical deactivation. This result may be of great importance since DNA damage in human cells was induced by $^1O_2$ photogenerated under UVA irradiation of fluoroquinolones.

Acknowledgments
The authors thanks the support of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Secretaría de Ciencia y Técnica, UNRC. (SECyT- UNRC).

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P68- Study of the degradation of the herbicide Isoxaflutole by different methods: Photo-Fenton and sensitized photolysis

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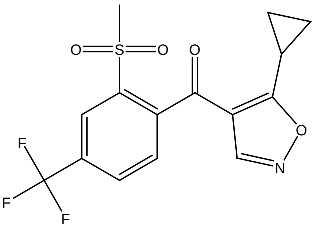

Fig. 1: Isoxaflutole (IXF)

Isoxaflutole (IXF, Figure 1) is a preemergent herbicide developed in relatively recent times. It is employed for the control of broadleaf weeds and weeds in maize. IXF exhibits a new mode of action: inhibits 4-hydroxyphenylpyruvate dioxygenase, an enzyme found in the pathway of carotenoid biosynthesis. IXF has a very short lifetime (8 to 18 days) and rapidly degrades into a stable and phytotoxic metabolite, diketonitrile (DKN). Further degradation of DKN produces a compound derived from benzoic acid (BA, 2-mesyl-4-trifluoromethyl benzoic acid) [1]. Although several studies have been carried out on the hydrolysis processes of IXF in solution and adsorbed on soils, no information has been found regarding possible photo-induced degradative processes.

The main objective of this work is to study IXF degradation by Fenton and FotoFenton from a kinetic-mechanistic point of view and to establish a comparison with results of the IXF photodegradation sensitized by Riboflavin (Rf).

Fenton and PhotoFenton: IXF showed reactivity with the $^{\bullet}$OH generated by FotoFenton in homogeneous medium, reaching conversions of almost 100%, with a pseudo-first order rate constant of 0.015 min^{-1}. During photolysis, photoproducts were detected by HPLC-UV-vis and the possible structures thereof were determined by HPLC-MS. One of the products is the benzoic acid derivative BA (see Figure 2) [2], a compound with low toxicity, which is which is currently produced in the degradation of IXF with NaClO [2]. The advantage of using the FotoFenton technique is the absence of chlorinated photoproducts.

Sensitized photodegradation: experiments of Rf-sensitized stationary photolysis (Rf) in the presence of IXFs, monitored by UV-Vis spectrophotometry, showed slight spectral changes, attributable to IXF degradation. These could be due to interactions of the IXF with the triplet excited state of Rf (^{3}Rf*) or reactive O$_2$ species (ROS) generated by Rf. Complementary experiences of laser flash photolysis, IR-close resolved phosphorescence and polarly-evaluated O$_2$ consumption, demonstrated that IXF deactivates electronically the excited triplet state of Rf with a rate constant of 1.46x10^7 M^{-1}s^{-1} and IXF is not degraded neither by singlet molecular oxygen ($O_2(^1\Delta_g)$) nor by superoxide radical ion ($O_2^{\bullet}$).

The photo-fenton process appears as the better option for IXF degradation due to the greater reactivity of $^{\bullet}$OH compared to ROS generated in the Rf photosensitized process.

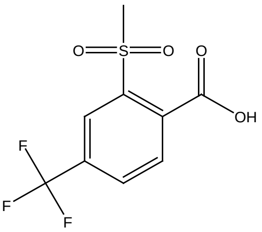

Fig. 2: Photoproduct (**BA**)

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P69-Gadusol protects tryptophan from photosensitized oxidation by pterin

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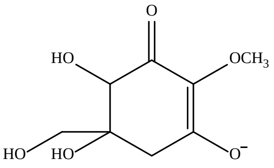
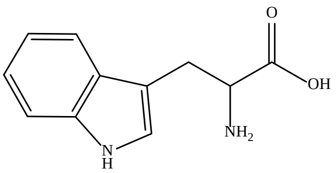
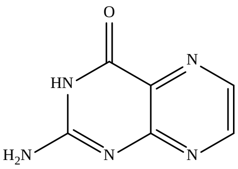
Pterins (Ptr) are heterocyclic compounds present in biological systems. They are considered photosensitizers that, under UV-A radiation, degrade DNA, proteins and their components. Thus, the study of defense mechanisms against these reactive species through the action of natural protective compounds has concentrated important attention. The mechanisms may imply: (i) inhibition of the formation of Ptr in excited state; (ii) deactivation of the excited states of Ptr; (iii) elimination of the reactive oxygen species (ROS) generated in the environment. Previously, the behavior of Ptr in the presence of the essential amino acid tryptophan (Trp) has been studied. The predominant photooxidation pathway of Trp is an electron transfer process from the amino acid to the Ptr triplet excited state.[1]



Gad



Trp



Ptr

Gadusol is a natural antioxidant that has been found to be associated with proteins in ocular lenses and in the skin of fish.[2] It has been established that its anionic form (gadusolate, Gad) is very efficient at neutralizing ROS and deactivating triplet excited states of sensitizers.[3-4] Therefore, it is interesting to study the effect of Gad on the oxidation mechanisms of amino acids in the presence of Ptr.

Gad was obtained from *Pseudopercis semifasciata* roes, according to the procedure reported by Plack *et al.* [5] and adapted by Arbeloa *et al.*.[3] Aereated aqueous solutions (pH 6.5) containing Trp, Gad and Ptr were irradiated at 350 ± 5 nm in a quartz cell of 1 cm optical path, at room temperature. Control experiments with solutions containing only Trp and Ptr, or Gad and Ptr, were carried out under the same conditions. The progress of the reaction was monitored by HPLC with UV detection at 282 nm. Both Trp and Gad concentrations decrease as a function of the irradiation time, whereas the Ptr concentration does not change within the analyzed period (60 min). In the presence of Ptr and Gad, the concentration of Trp drops around 20% but, in the absence of Gad, the amino acid dissapears faster (*ca.* 61%). However, in deareated solutions containing Ptr and Gad no significant changes were observed in the absorption after irradiation for more than 180 min. This behavior is similar to that found for Trp-Ptr solutions in the absence of O_2, indicating that Ptr photosensitizes the oxidation of Trp in the presence of O_2.[1] Ours results suggest that Gad protects Trp from the photosensitized oxidation by Ptr. Therefore, further studies should be directed to explore potential applications of this marine metabolite in the treatment of skin disorders where Ptr is pathologically accumulated.

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P70- The Influence of Intense Magnetic Fields on the Rate of Relaxation of Excited States of Cr(III) Complexes.

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Magnetic fields can alter the speed, yield or product distribution of chemical reactions [1]. Although significant differences have been reported in the mechanisms by which the magnetic field disturbs the reaction rates of coordination complexes and the mechanisms that apply to reactions between radicals or excited states of organic molecules, the measurement and analysis of the effect of magnetic fields have provided information on the reactivity, structure and movement of the species subjected to its effects. Intense magnetic fields ($B > 5T$) can modify the photoreactivity of transition metal complexes, generating changes in emission spectra, relaxation of excited state, quantum reaction yields and quenching processes [2] .

In this work we present the results obtained on the effects of intense magnetic field ($B\approx$ 0-10 T) on the kinetics of deactivation of Cr (III) complexes with polypyridine ligands. The magnetic field in the reaction cell is generated with a home made system consisting in a high voltage capacitor, an electric coil and triggering electronics. The magnetic pulse is coupled to a Nd-YAG laser (Brillant-B, Quantel) operating at 355 nm. Lifetimes ($\tau_0 = 1/k^0_{nr}$) of the excited states of the complexes ($^2T/^2E$) $[Cr(phen)_3]^{3+}$ were measured in aerated solutions at room temperature (phosphate buffer pH = 8.0; NaCl 0.1 M) in the absence and presence of applied magnetic field (B = 2, 4, 6 and 8 T) obtaining the lifetimes shown in Table 1 and Figure 1.

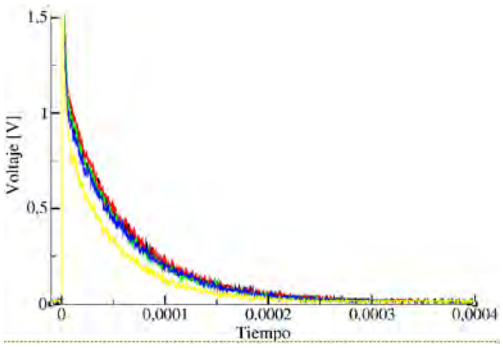
Figura 1: ECM sobre el tiempo de vida de fosforescencia ($^2T/^2E$)$[Cr(phen)_3]^{3+}$

Complejo	τ_0 [μs] (B=0 T)	τ_0 [μs] (B=2 T)	τ_0 [μs] (B=4 T)	τ_0 [μs] (B=6 T)	τ_0 [μs] (B=8 T)
$(Cr(phen)_3)^{3+}$	60,3	56,2	52,5	50,1	48,9

Tabla1 : Tiempo de vida de fosforescencia del ($^2T/^2E$)$[Cr(phen)^3]^{3+}$ con ECM

Acknowledgments: This work has been supported by Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, CONICET, ANPCyT and MinCyT.

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P71- Magnetic nanocomposites as photocatalyts for Carbamazepine degradation

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Generally, nanostructured copper and iron bimetals possess unique photocatalytic and magnetic properties in, for instance, environmental remediation. In particular, the nanosize copper and iron bimetal photocatalysts encapsulated in a robust carbon-shell can be a promising option [1].

We have prepared here different types of magnetic materials using bio-based substances (BBS) obtained from composted urban biowaste [2] to complex Fe^{+3}/M^{+2} ions. The complexes were then subjected to thermal treatment under nitrogen atmosphere to develop magnetic phases. By varying the temperature of the heating treatment (400, 600 and 800ºC), and the M^{2+} ion (Fe^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}), different materials were obtained. After a full characterization they were used to photodegrade Carbamazepine (CBZ), an antiepileptic drug commonly found in natural waters [3].

In a typical experiment, 100 mL suspensions of 2 mg L^{-1} of CBZ and 0.625 g L^{-1} of the particles were irradiated with constant stirring in a Rayonet RPR-3500 reactor equipped with 8 lamps with a maximum emission centered at 300 nm. The remnant concentration of CBZ at different irradiation times was monitored by HPLC after magnetic separation of the nanoparticles.

We found that for the Fe/Cu materials the amount of CBZ photodegraded after six hours of irradiation was strongly dependent on the temperature reached during the heating treatment for the synthesis of the nanomaterial. The CBZ photodegradation (ca. 80%) was the highest for the samples treated at 600ºC, whereas it was only 40% for the material treated at 400ºC. Comparison of data with the series of nanocatalysts obtained using different M^{2+} ions and the thermal treatment at 600ºC showed that the highest percentage of CBZ degradation (ca.90% after 3h) was obtained for the material made from Fe^{2+} and Fe^{3+}, whereas in the other cases only ca. of 80% degradation was achieved after 5h. These differences are interpreted in terms of the structure and crystalline phases of the materials.

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P72- Upconversion: Towards goal-oriented UCNP design

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Lanthanide ions have remarkable photophysical characteristics due to their internal enegy levels. In particular, they have a large anti stokes efficiency through upconversion (UC). In this process, multiple low energy photons (typically NIR) are sequentially absorbed and such energy is then reemited from long lived states (μs-ms) as higher energy radiation (visible or UV). NIR excitation light not only allows for deeper light penetration and reduced photodamage effects, but also offers lower autofluorescence, reduced light scattering, and phototoxicity. Lanthanide-doped upconversion nanoparticles (UCNPs) are therefore a promising new generation agents for biosensing and bioimaging, but their photophysics is still under study.

Rare earth trivalent ions embedded in an inorganic host (β-$NaYF_4$: 20%Yb^{3+}, 2%Er^{3+}) were synthesized via thermal techniques [2]. Hexagonal phase UCNPs with sizes ranging from 15 to 800 nm were obtained and characterized by XRD and SEM techniques.

The emission spectra of the samples were measured with a commercial spectrofluorometer modified to use a 980 nm pulsed excitation source coupled with a time resolved detection system. This new arrangement facilitated the simultaneous measurement of the stationary emission spectra as well as the spectrally resolved excited state lifetimes of the samples (See Figure 1).

The advantage to observe both the stationary and dynamic behavior of the system *in situ*, offers the possibility to perform combined studies to measure the dependence of the intensities of the emission maxima and the excited state lifetimes on the excitation pump power in different dispersion media for different samples.

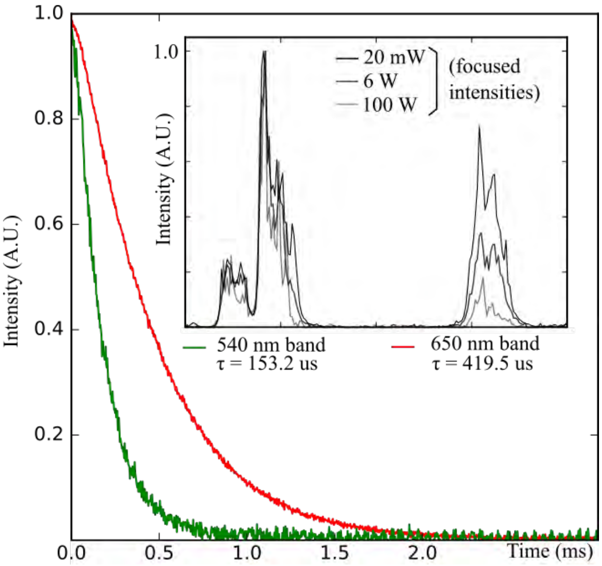

Figure 1: UCNPs emission spectra and decay curves of the excited states monitored at 540 nm and 650 nm.

In particular, the variation of the ratio of the intensities of the green (520-560 nm) to red (630-670 nm) emission bands together with their respective excited state lifetimes as a function of the incident power, provided valuable information regarding the non-linear relationship between absorbed and emitted light power (quantum yield). These results are essential to elucidate how the competition process between the linear decay rate and the upconverted rate at the intermediate states takes place to get a better insight about the dynamics of the intra f-f transitions of the lanthanides for different power regimes enabling goal-oriented UCNP design.

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P73- Fluorescent Folic Acid-PEG modified silica nanoparticles for the study of aggregation in tumour cells by Fluorescent Correlation Spectroscopy (FCS)

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Targeted delivery of nano systems has to deal with the following issues: a) pharmacological drug carriers must be designed in such a way that the release rate of the encapsulated drug can be controlled and b) controlling the specific interactions between the carrier and the cell membrane receptors at the molecular level [1]. Therefore, it is important to minimize unspecific binding events in order to favour the attachment/interactions with the target tissues/cells. Molecules with anti-fouling properties such as poly(ethylene glycol) (PEG), which prevents the recognition of the particles by the RES (reticuloendothelial system), are often used as a spacer between the particle surface and the recognition function. In fact, a hydrophilic coating with PEG and allows, depending on the nanoparticle size, to reach the desired site [2, 3].On the other hand, folic acid (FA) shows extremely high affinity to the folate receptors (FRs) which are normally overexpressed in tumour tissues. Thus, FA grafted nanoparticles (NP) can be used to specifically target tumour tissues.

In this work, we designed, synthesized and characterized small size (~40 nm) well monodisperse fluorescent silica NP (ATTO@SiO_2) by a modification of the Stöber method (Fig. 1). We also prepared different FA-PEG polymers to graft the surface of ATTO@SiO_2 NP. The aim of preparing [ATTO@SiO_2]-PEG) NP is to study how these systems affect the aggregation process in tumour cells by FCS [4]. We found that ATTO@SiO_2 NP were successfully internalized by A549 cells and showed response in the observation by FCS.

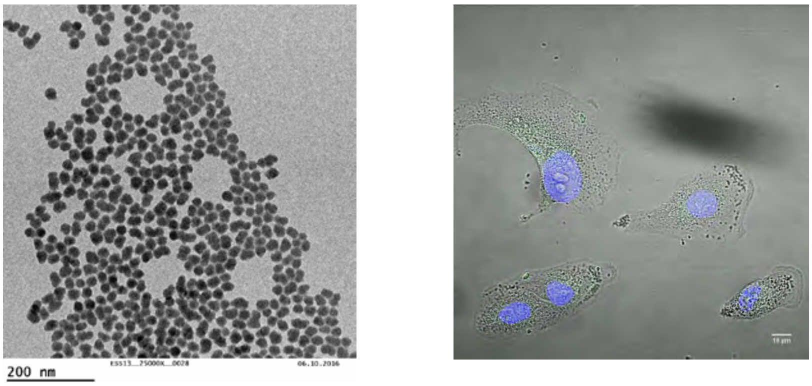

Fig. 1. Left: TEM image of ATTO@SiO_2 NP; Right: DIC and fluorescent confocal image of A549 cells (10 minutes of incubation with ATTO@SiO_2 NP).

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P74- Cavitands: Photophysical properties vs. substituents

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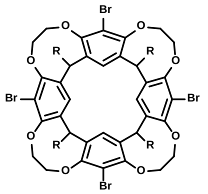

Figure 1: *Tetra*-bromine cavitand

Methylene-bridged resorcinarenes or 'cavitands' (Figure 1) are macrocycles with rigid structures and extensive applications [1]. They are unique bowl-shaped macrocyclic compounds that can be prepared with reasonable to high yields from the condensation of resorcinol and aldehydes, without using templates [2].

The goal of this study is to obtain cavitands with different photophysical properties in function of the number and the nature of substituents.

Photoinduced reactions with benzenethiol or 4-methoxybenzenethiol as nucleophiles render *mono-*, *di-*, *tri-* and *tetra*-substituted cavitands in good yields, but it is just obtained *mono*-substitutions products with 2-mercaptopyridine (with different retentions of bromine).

The absorption and fluorescence properties for all products was studied. In figure 2, the most relevant absorption and emission spectra are presented.

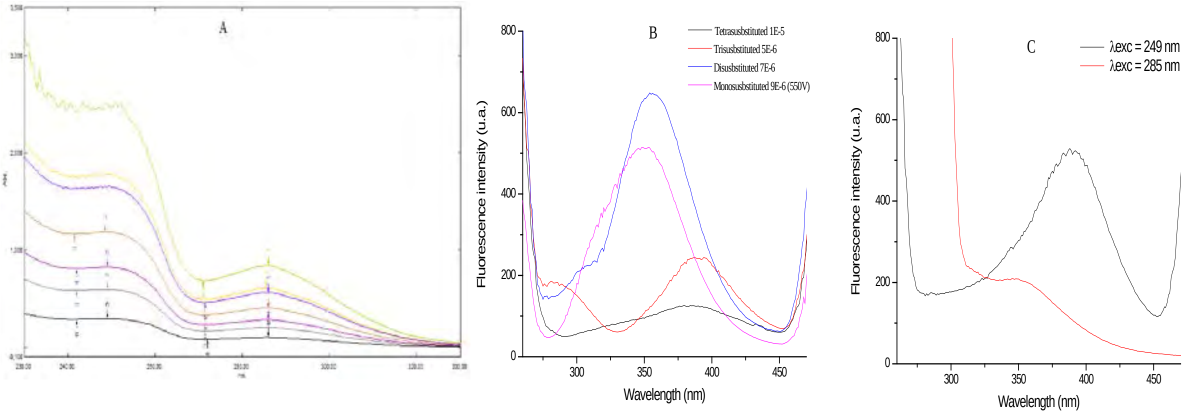

Figure 2: (A) Absorption spectra of *tetra*-substituted cavitand with 4-methoxybenzenethiol. (B) Emission spectra of all the products with 4-methoxybenzenethiol in CH_3CN (λexc = 249 nm). (C) Emission spectra of *mono*-substituted *tri*-bromine cavitand with 2-mercaptopyridine in CH_3CN.

In summary, a change in absorption, emission and fluorescence intensity it is observed when the nature and the number of substitution are modified.

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P75- Photochemical properties of hepta-coordinated tin(IV) complexes.

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Organotin(IV) complexes have gained recognition because of their remarkable biological applications; their industrial potential, and the ability of tin to form stable bonds both with carbon as well as with heteroatoms. As one of the representative organotin(IV) compounds, carboxylates have called attention in the last few decades due to their broad use as catalysts, stabilizers, antimicrobial, anti-inflammatory, antifungal, and antituberculosis agents [1,2]. Having synthesized some novel hepta-coordinated complexes, in this work we present the first study about their photochemical properties. Our goal was to characterize their behavior when a 254 nm photon is absorbed. The different paths that the excited state will follow, was proved under different conditions (solvents, presence or absence of molecular oxygen, temperature, etc.).

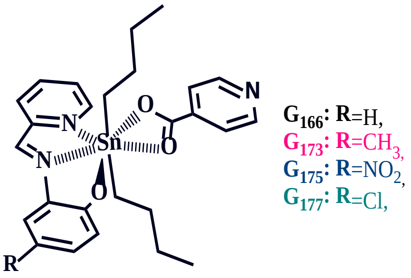

Figure 1. Heptacoordinated Organotin (IV) Complexes

We recorded UV-Vis as well as fluorescence emission spectra (figure 2 **a** and **b**) that were further analyzed. Though the complexes studied show all considerable molar absorptivity coefficients (ε, figure **2a**) in acetonitrile (ACN), our results show that, the fluorescence quantum yields (calculated relative to the reference tris-(bipyridine)-ruthenium(II) chloride) ranged between 0.1 to 2.3 10^{-2}. Other processes, like photo-degradation, are occurring. We measured the rate constant coefficients for the disappearance under different temperatures and solvents. In all cases, the processes are first order and independent of temperature. Furthermore, the rate coefficients were compared in the presence as well as in the absence of O_2, to discern whether an intersystem crossing to the triplet state is operative (see table 1). As it is well known, O_2 can act as an efficient quencher in photodegradation reactions. Nevertheless, no quenching was observed for these tin compounds. Finally, all photoproducts were identified unequivocally through NMR and CG-MS analysis.

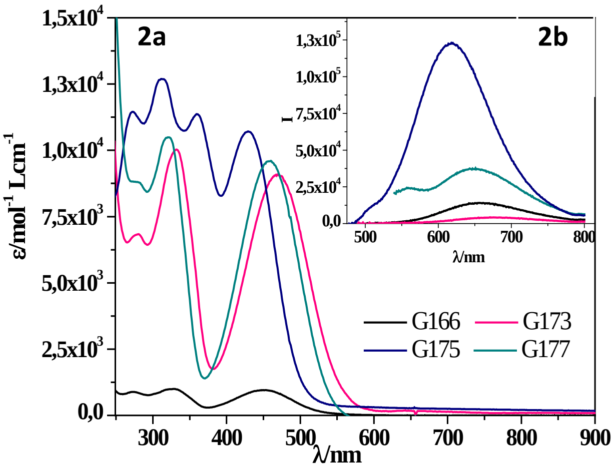

Figure 2. **a)** UV-Vis spectra; **b)** Fluorescence emission spectra of heptacoordinated Organotin (IV) Complexes

Complexes	$k_{254nm}N_2$	$k_{254nm}O_2$	$T_{1/2}$/s
G166	2,74 10^{-03}	1.11 10^{-03}	624.45
G173	2.85 10^{-03}	1.00 10^{-03}	693.15
G175	1.88 10^{-03}	6.72 10^{-04}	1031.47
G177	6.63 10^{-03}	1.50 10^{-03}	462.10

Table 1. Rate constants measured in ACN at 298 K

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P76- Excited State Dynamics of Cold Protonated Cytosine Tautomers: Characterization of Charge Transfer, Inter System Crossing and Internal Conversion Processes

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Charge transfer reactions are ubiquitous in chemical reactivity and often viewed as ultrafast processes. For deoxyribonucleic acid (DNA), femtochemistry has undeniably revealed the primary stage of the deactivation dynamics of the locally excited state following electronic excitation while longer time scales could hardly be investigated within the experimental time window. We here demonstrate that the complete excited state dynamics can be followed from a few femtoseconds up to milliseconds through an original pump-probe photodissociation scheme applied to cryogenic ion spectroscopy with picosecond and nanosecond pulse lasers. Excited state calculations at the RI-CC2 level were also performed in order to help the interpretation of the experimental results.

Two tautomers of protonated cytosine were spectroscopically observed: the enol tautomer, in which the H^+ is bonded to the C=O group of Cyt and the keto tautomer in which the H^+ is bonded to N3 of cytosine.[1] The excited state dynamics shows that in both tautormers the locally excited $^1\pi\pi^*$ state decays in the femtosecond range towards long-lived charge transfer state and triplet state with lifetimes ranging from microseconds to milliseconds. A three-step mechanism ($^1\pi\pi^* \rightarrow {}^1CT \rightarrow {}^3\pi\pi^*$) is proposed where internal conversion from each state can occur leading ultimately to fragmentation in the ground electronic state (Figure 1).

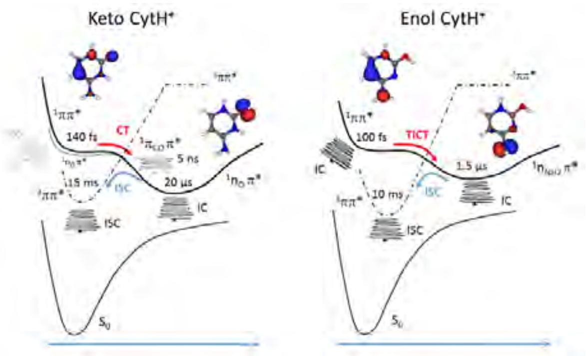

Figure 1. Schematic Potential Energy Surfaces, excited state lifetimes and proposed deactivation mechanisms to the ground state for keto and enol protonated cytosine.

Acknowledgments:
This work has been conducted under the International Associated Laboratory LIA/LEMIR with financial supports of CNRS, GDR, EMIE, CONICET, SeCyT-UNC and FonCyT. We acknowledge the use of the computing facility clustersMésoLUM of the LUMAT federation (FRLUMAT 2764) and MAGI of the University Paris 13.

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P77- New aza-boron-dipyrromethene compound for single molecule fluorescence studies in cells

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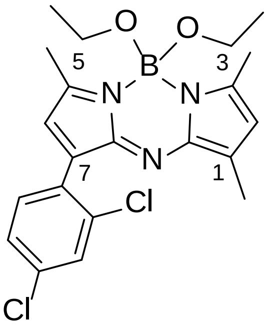
Corticotropin-releasing hormone (CRH) is a key protein involved in neuroendocrine response to stress [1]. There is a widespread interest in understanding the molecular behavior of CRH type 1 receptor (CRHR1), as it plays a primary role in regulatory mechanisms. Owing to the lack of reliable specific antibodies for CRHR1, studying its dynamics and distribution by fluorescence microscopy requires a different labeling strategy. A set of novel fluorescent antagonists have been designed for this purpose. Based on non-fluorescent reported antagonists and structure of CRHR1 [2], a backbone based on an aza-boron-dipyrromethene (aza-BODIPY) structure was chosen for a docking study. The software used for docking studies was *Internal Coordinates Mechanics* (ICM), and a flexible ligand-rigid receptor approach was performed. Aza-BODIPYs are suitable for single molecule fluorescence microscopy (SMFM), due to their high photostability and emission brightness. Substitution to provide adequate photochemical stability was also taken into account.

Compound **1** was chosen as the first one to be synthesized. Its precursor, **2**, has been successfully synthesized and its spectroscopic properties were measured.



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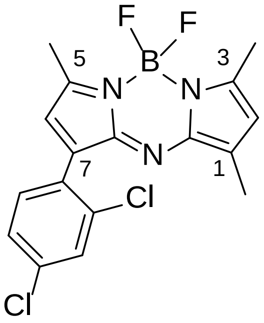

2

Compound **2** is an asymmetric aza-BODIPY with only one aromatic substituent in 1, 7, 3 and 5 positions. There are no aza-BODIPYs with this characteristics described in literature. It displays negative solvatochromism, and its emission quantum yield is around 0.80, with a lifetime of 3.9 ns. **2** also shows antagonist activity in biochemical assays. In STORM (*Stochastic Optical Reconstruction Microscopy*) experiments carried out in fixed hippocampal cells expressing CRHR1, **2** demonstrated a blinking and brightness performance comparable to Alexa647, one of the most frequent dyes used in this technique. Live cells experiments showed a short-time dye incorporation inside cells, and an exponential decrease of emission from cells, arriving to a plateau after 13 hours. This may coincide with specific binding between **2** and CRHR1.

These results indicate that **2** may be considered as an adequate fluorescent antagonist for CRHR1, and that it is a proper dye for single molecule experiments, as for super-resolution microscopy.

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P78- Modification of the response to ALA-PDT by hydrogen sulfide (H_2S)

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Photodynamic Therapy (PDT) is a treatment for cancer, that combines a photosensitizer (PS) and light. When the light reaches the PS, it is excited, and triggers a series of reactions that generate reactive oxygen species (ROS), killing the cells[1]. Our group has been focused on the study of the pro-PS, 5-aminolevulinic acid (ALA), that leads to the synthesis of the PS Protoporphyrin IX (PpIX), inside the cell. PpIX is accumulated preferentially in cancer cells, and exerts its cytotoxic effect upon illumination. Hydrogen sulfide (H_2S) is a molecule that belongs to the gasotransmitters family, along with the nitric oxide (NO) and carbon monoxide (CO). These molecules can freely diffuse through biological membranes and act as messengers in signaling pathways[2]. H_2S is produced endogenously by 3 enzymes (CBS, CGL, CAT/3MST), and it is involved in a variety of physiological processes, such as vasodilatation, inflammation, cellular cycle and neuromodulation[3]. Especially, it is supposed to have a cytoprotective effect[4], although the mechanisms are almost unknown.

The aim of this work is to study the effect of the H_2S on ALA-PDT treatment.

The LM2 cell line (mammary murine tumor, Roffo Institute, Argentina) was treated with ALA-PDT and H_2S was added at different time points of the treatment (24 h before irradiation, coincubated with 1 mM ALA; during irradiation; post-PDT, and the combination of the three conditions).

Without H_2S, lethal light dose 50 (LD_{50}) was 114 mJ/cm2; with H_2S during irradiation, LD_{50} was 116 mJ/cm^2; with H_2S post PDT, LD_{50} was 152 mJ/cm2; with H_2S coincubated with ALA, LD_{50} was 304 mJ/cm^2 and with H_2S at every point of PDT, LD_{50} was not achieved even at the highest dose applied.

Those results show that H_2S induced a decrease in cells sensitivity to PDT. Parallel experiements employing ovary and macrophage cell lines (SKOV-3, IGROV-1 and Raw 264.7) were carried out and the same effect was observed.

PpIX was extracted from cells after incubation with ALA or ALA+H_2S, and then measured fluorometrically. In all cell lines, PpIX synthesis was inhibited by 10 mM H_2S, 53% in LM2; 55,6% in SKOV-3; 81,2% in IGROV-1 and 32,8% in Raw 264.7.

The amount of glutathione (GSH) was measured in LM2 cells after exposure to 10 mM H_2S (2 and 24 h before the measurement) and a slight but significant increase in GSH levels was observed in cells that have been exposed to H_2S (control:73 and treatment:84 nmoles/10^6 cells).

The direct effect of H_2S as ROS scavenger was also measured, and it was found that ROS levels decreased when H_2S concentration was increased.

The activity of 2 enzymes involved in PpIX biosynthesis, ALA-dehydrase (ALA-D) and porphobilinogen deaminase (PBG-D), in fresh blood erythrocytes, was measured after incubation with different concentrations of H_2S. ALA-D activity decreased 38% with the lowest H_2S concentration (10 μM) and PBG-D activity was not modified by H_2S at any concentration (up to 10 mM).

Our results show that H_2S produces a protective effect on the PDT treatment and it could be due to many factors: the increase of antioxidant state of the cell, the direct scavenging of ROS, and the decrease of the PpIX biosynthesis. These results should be taken into account since several tissues produce high levels of H_2S and they could have a differential response to PDT, and in addition, these findings would help improve the PDT efficiency.

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P79- FOLLOWING LIPID PEROXIDATION: A SINGLE BACTERIA IMAGING STUDY

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Lipid peroxidation (LP) is a crucial step in the pathogenesis of several disease states. This is a self-propagating chain-reaction process initiated by reactive oxygen species (ROS). Oxidation of lipid molecules affects membranes properties jeopardizing cells viability. ROS are not only produced in cells as part of the respiratory chain, different drugs for instance bactericidal antibiotics induces LP accelerating cellular respiration and consequently enhancing ROS production.

The goal of our work was to assess the LP process caused by Ciprofloxacin in a Gram-negative strain, *Escherichia coli* ATCC 25922. We evaluated oxidative damage in real time through a sensitive fluorogenic probe H_2B-PMHC. This probe was developed and characterized by the group of Prof. Cosa; it presents high specificity toward lipid peroxyl radicals, the dominant reactive oxygen species encountered in lipid membranes under oxidative stress.

To learn on the physiological role of antibiotics at the single bacterial level we focused on fluorescence imaging experiments upon excitation with an evanescent beam in a Total Internal Reflection Fluorescence Microscope (TIRFM). The sample was incubated with increasing antibiotic doses (3, 30, 100 μM) for 12 h monitoring intensity vs. time profiles. Our experiments revealed that LP is a drug concentration-dependent process in *E. coli* strain. We will also discuss phenotypic heterogeneity in individual bacterium such as e.g.: the time each bacterium increases ROS production (following fluorescence enhancement), the amount of ROS being produced and dye distribution. Furthermore, a cell viability assay was assessed using a death marker (propidium iodine-PI), enabling quantification of dead bacteria from the beginning till the end of the assay.

We reasoned that the observed differences could be due to the metabolic stages of each bacillus indicating that bacteria with a high fluorescent at the beginning of the experiments were probably in an early dead phase.

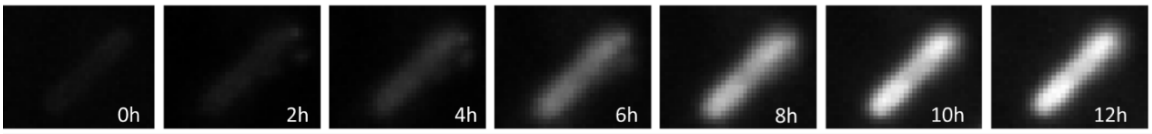

Figure 1. *E.coli* treated with 100 μM of ciprofloxacin and the fluorogenic probe H_2B-PMHC

P80- Excited State Intramolecular Proton Transfer (ESIPT) to Aromatic C-atom: Influence of Substitution on *o*-Phenylphenol

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Excited State Intramolecular Proton Transfer (ESIPT) is an ultrafast process in which an acidic proton is transferred to a basic site within the same molecule on photoexcitation. The most common acidic groups in ESIPT are the phenolic OH or the amine NH, and the usual basic site is a heterocyclic nitrogen, or carbonyl oxygen. Besides the typical cases, there are systems in which a carbon atom acts as the proton acceptor, but these examples are quite rare. However, they are particularly interesting since these reactions generate quinone methide intermediates (QMs) (Figure 1). QMs are involved in various processes such as polymerization, DNA alkylation, lignification in plants, among others [1].

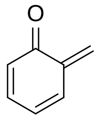
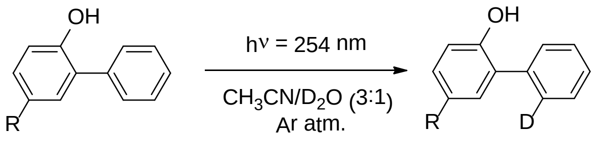


Figure 1. *o*-QM

P. Wan *et al.* have widely studied the generation of QMs *via* ESIPT from phenolic OH to the corresponding C-atoms in different hydroxybiaryl systems [2]. One of the first examples reported was the model case of *o*-phenylphenol, in which the proton is transferred to the 2-carbon position of the phenyl ring not containing the phenol, in the excited state. An easy manner to follow the ESIPT process consists in carrying out the photostimulation in deuterated protic solvents, this allows to recover the starting material isotopically labeled in the positions of the molecule that received the transferred deuteron in excited state [3].

In order to contribute to the understanding of QMs generation in the above mentioned systems, the goal of this study is to analyse the impact electron-donating and withdrawing substituents have on the ESIPT efficiency of *o*-phenylphenol. For this purpose, compounds **1-5** were synthetized and purified following previously published procedures. Irradiation of CH_3CN-D_2O solutions of **1-5** under 254 nm light was performed and the extent of deuterium (D) exchange was measured by ^{1}H NMR (Figure 2). It was found a linear correlation between the electronic nature of substituents and the efficacy of the process. As is shown in Figure 3, D-incorporation rises as the donating character of substituent increases, whereas the ESIPT is almost negligible when the substituent is a strong electron withdrawing group. Further studies are currently undergoing in order to evaluate the effect of substitution in the phenyl ring of the *o*-phenylphenol. In addition, photoacidity of the studied compounds will be considered to gain a deeper insight in the global operating mechanism.



R = OCH_3 (**1**), $C(CH_3)_3$ (**2**), H (**3**), COOH (**4**), CN (**5**)

Figure 2. Photolysis of *p*-substituted *o*-phenylphenols.

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P81- Photophysic implications of multiple dye-labelling to a polyelectrolyte

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Polyelectrolytes have attracted increasing interest in the last decades due to its assiduous use in layer by layer self-assembled structures, which have multiple applications spanning surfaces modification (electrodes or nanoparticles),[1] controlled drug-delivery[2] and formation of microcapsule structures,[3] among others. Commonly the polyelectrolytes can be modified or functionalized with photochemically active molecules to confer additional photophysical properties of interest. Dyes attached to polyelectrolytes have been used for energy transfer processes in layer-by-layer self-assembled nanostructures that mimic antenna systems,[4] as gold nanoparticle coatings in fluorescence enhancement experiments by plasmon interaction,[5] and for the controlled release of genes.[6] However, despite the multiple use of polyelectrolytes covalently labeled with dyes, the literature on the physicochemical and photochemical behavior of these systems is scarce. More importantly, there is little information about how the intermolecular forces beween multiple dye molecules, or between dye molecules and the polymer backbone, affect the labelled polymer conformation in solution, or when it is deposited on a substrate.

The present study aims to establish the influence of some chemical and physicochemical parameters - such as the degree of substitution in the polymer chain, hydrophobicity and charge of the dyes - on the conformational and photophysical properties of the macromolecules. For these purposes, the synthesis of a dye (rhodamine B isotiocyanate – RITC) with a polyelectrolyte (poliallylamine hidrochloride, 450 kD – PAH) was carried out under an initial stechiometric dye to monomer relationship of 0.02. The concentration of PAH for the synthesis (~0.01M in monomers) was carefully selected by means of Dynamic Ligth Scatering (DLS) measurements to ensure the presence of isolated chains in solution. Samples were purified by dialisis and exclusion chromatography using Sephadex™ G-25 M pre-packed colums. After purification, the dye content or polymer molecule was rougly estimated, by absorption spectroscopy, as ~96.

UV-absorption and steay-state fluorescence studies on water RITC-PAH solutions indicate that the dye aggregation (with non-fluorescent aggregates) far exceeds 50%. The fluorescence anisotropy of PAH-RITC is ~ 0, showing free rotation of the dye in the polyelectrolyte structure. Fluorescence microscopy experiments on dry RITC-PAH on a coverslip shows approximately 6 molecules of dye, on average, for each polimer unit. Probably, dried condition strongly increase the dye aggregation compared with aqueous enviroment. Fluorescence correlation studies (FCS) of the labelled polymer solutions show the presence of free rodamine-B dye (54 μs and hydrodynamic radius of 3.25 Å) and coiled RITC-PAH molecules (5000 μs and hydrodynamic radius of 55.7 nm). A comparison of the hydrodynamic radius for pure PAH obtained by DLS (~80 nm) with the results of FCS allows us to infer that the aggregation of the dye, due to hydrophobic interactions, plays a key role reducing the radius of the coiled conformation of the polielectrolyte. We posit that the dye-to-dye interaction is responsible of intramolecular label aggregation which forces the polymer backbone to a structure much more compact than that for an unlabelled polymer.

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P82- Comparison of photophysical properties of two zinc (II) phthalocyanines in dimethylformamide or into liposomes

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Photodynamic therapy (PDT) utilizes light in combination with a photosensitizing agent to induce several phototoxic reactions. Both components are innocuous if they act separately but in combination, are able to induce injury and cellular death [1]. Photodynamic reaction involves a light absorption by a photosensitizer to excite the molecule to the excited singlet state. This excited state undergoes intersystem crossing to the long-lived triplet state, which can react with molecular oxygen inducing reactive species such as singlet oxygen, superoxide, and radicals. These reactive species can oxidize the surrounding bioorganic molecules leading to cell death [2].

Phthalocyanines (Pcs), second generation photosensitizers, are characterized with far red wavelength absorption (>670 nm), long triplet life time (~1 ms), and high quantum yields of singlet oxygen generation (>0.2) [3]. Pcs have been used as a treatment for a variety of cancers and non oncological applications, such as actinic keratosis and mycosis fungoides.

Due to hydrophobic character of Pcs, intravenous treatment is greatly hampered. Liposomal preparations are currently used as an effective delivery system in experimental studies and clinical trials [4].

In this work the photophysical properties of two Pcs (ZnPc and TAZnPc) in DMF (dimethylformamide) solution or carried into DipalmitoylPhosphatidylCholine (DPPC)-cholesterol liposomes in PBS (Phosphate Buffer Saline) and their effectiveness on glioblastoma cells were evaluated. *In vitro* studies were performed using Dulbecco's Modified Eagle's Medium (DMEM) supplemented with Fetal Bovine Serum (FBS) as cell culture.

In DMF, absorption spectra UV-Vis for TAZnPc presents a higher red-shifted λ_{max} (702 nm) compared to ZnPc (670 nm). Fluorescence of ZnPc: λ_{ex}:640 nm, λ_{em}:675 nm, TAZnPc λ_{ex}:670 nm, λ_{em}:711 nm. Regarding singlet oxygen production in DMF, TAZnPc presents a Φ_{Δ} of 0.45, similar to that of non-modified ZnPc (0.56). In liposomes formulation didn´t show shift in wavelength absorption and emmision.

DMF solutions as well as liposomes were diluted in DMEM and DMEM/FBS. Fluorescence and UV-Vis mesurements presented only changes in the intensity of absorbtion or emmision.

In *in vitro* studies both Pcs show an increase in their photosensitizing activity when they were administrated in DPPC-cholesterol liposomes rather than in DMF.

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P83- Photochemical and photophysical behavior of 2-halo-*N, N*-arylylaniline in photostimulated intramolecular arylation reactions. Synthesis of carbazoles.

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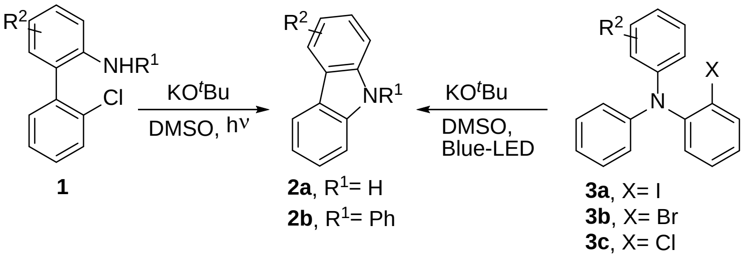
Recently we reported an efficient strategy to afford a family of 9-*H*-carbazoles (**2a**) by a photosubstitution intramolecular *N*-arylation reaction from biphenyl amines (**1**) (Radical Nucleophilic Substitution Unimolecular, $S_{RN}1$) (Scheme 1) [1]. In contrast to C-N bond formation strategies to obtain carbazoles, C-C bond forming route from 2-halo-*N,N*-arylaniline (**3**), has been less explored. More recently, the reactions of 2-iodo and 2-bromodiarylanilines (**3a** and **3b**) with KO^{t}Bu in presence of ethylene glycol or 1,10-phenanthroline provide carbazoles in moderate to excellent yields by Base-promoted Homolytic Aromatic Substitution [2]. In contrast to iodide and bromide substrates (**3a** and **3b**), chloride derivative **3c** exhibit lower reactivity. In our case, when we did the photostimulated reaction (using visible light) of **3c** (R^2= H) in presence of KO^{t}Bu (3 equiv) in DMSO we succesfully obtained **2b** in 85% yield.



Scheme 1. Synthesis of carbazoles **2a-b** by C-C or C-N bond formation from biphenyl amines (**1**) and 2-halo-*N, N*-diarylaniline (**3**), respectively.

Under this super-basic conditions, dimsyl anion is formed from a strong base (KO^{t}Bu) and DMSO (solvent). Preliminar results reveal that no Charge Transfer Complex (CTC) interaction could be detected by the UV-Vis absorption spectrum between the dimsyl anion and **3.** Previous studies showed that dimsyl anion is responsible for inducing the initiation by a photo-BHAS process on alkyl and aryl halides [3]. This posibilitty was analized, however there was not change in fluorescence intensity of **3c** increasing concentrations of KO^{t}Bu, what is more a new maxima of the emission spectra was detected. In the present work we study the photophysical properties (UV-Vis, steady state fluorescence and time-resolved fluorescence) from 2-halo-*N, N*-diarylaniline and photochemical aspects in the mechanism (varying the reaction conditions) of these photosubstitution reactions. Also, computational modelling will be use to evaluate the proposed hypothesis in order to make a complete mechanistic picture of this cyclization reaction.

Acknowledgments

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P84-Photodegradation of crude oil in tetrachloroethylene

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Due to the environment contamination by petroleum-based products, guidelines and regulations for public health protection and analytical methods are periodically updated. The amount of total petroleum hydrocarbons (TPH) found in a sample is useful as a general indicator of petroleum contamination in soil, water or air. TPH describes a mixture of chemical compounds that originally come from crude oil.

A well-known method for determination of TPH was EPA 418.1 [1-2], which measured the IR absorbance of the C–H bond employing CFC-113 as the extraction solvent. Tetrachoroethylene (TCE), a rather non-volatile nonhydrocarbon solvent with infrared transparency, was found to be a suitable replacement to CFC-113. In this method, a representative crude oil sample should be selected and used for calibration.

In order to study the photostability of petroleum in TCE, a solution of a heavy crude oil from San Jorge Gulf basin (Bella Vista Oeste field) was exposed to UV-A radiation.

Different modes of fluorescence spectroscopy (conventional, synchronous and total fluorescence spectra, EEM) were carried out employing a Jasco FP6200 steady-state fluorometer. Fluorescence emission spectra was recorded at an excitation wavelength of 360 nm and synchronous fluorescence spectra were obtained between 300 and 600 nm ($\Delta\lambda$= 25 nm). A Horiba OCMA-3RA IR spectrometer was used for TPH measurements at 2930 cm^{-1}. One sample was kept in the dark for control.

Degradation of fluorescent compounds of crude oil (> 70 %) was achieved after 90 minutes of irradiation, while only 5 % of TPH were consumed. No changes were observed in the control sample.

The results obtained show that the heavy crude oil employed in this study is photodegraded in TCE and allow to infer information about the storage conditions of the calibration samples used for TPH determination.

Acknowledgments. NSC thanks PM-Q (Proyecto Estratégico de Mejora de Química-Programa de Calidad Universitaria de la Secretaría de Políticas Universitarias del Ministerio de Educación) for a scholarship.

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P85- Antagonism between Resveratrol and antimicrobial agents

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Several antimicrobial agents, such as antibiotics and sensitizers used in photodynamic therapy, are efficient to generate reactive oxygen species (ROS) in order to eliminate undesired pathogenic microorganisms that are harmful to health.

Among natural antioxidants reverastrol (RSV) is efficient to prevent damage from ROS. However, the consequences of the administration of RSV during an antimicrobial treatment are unknown. To investigate possible antagonistic or synergistic effects of RSV during antibiotic therapy (levofloxacin, LVX) or a photodynamic inactivation (PDI) therapy (visible radiation and methylene blue, MB), the elimination of *Staphyloccocus aureus* of a planktonic culture was evaluated in the presence of RSV.

Results show that the antimicrobial capacity of these therapies is significantly diminished when LVX or MB are co-administered with RSV. In the case of LVX, the presence of RSV increases 20-fold the bacterial survival compared with LVX (0.125 µg/ml) alone. Moreover co-administration of both MB and RSV decrease MB efficacy, which improve bacteria survival from 10 to 1000-fold in the whole range of MB concentration tested (6.25 to 50 µg/ml).

The results presented in this work indicate that the consumption of RSV during an antimicrobial treatment is strongly discouraged. Finally, considering that the microbiocidal activity of host defenses (neutrophils, macrophages) is also mediated by ROS, the topical addition of RSV, may also affect the normal control of pathogens of the human body. Therefore this work highlight the importance of the evaluation of possible antagonistic effect when an antimicrobial agent with ROS-mediated action is co-administrated with RSV.

Acknowledgements

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P86- Photoreduction of Ag^+ in the presence of lysozyme produces stable hybrid nanoparticles (AgNP@LZ) without bactericidal effect

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In recent years the microbial resistance to conventional antibiotics has increased, being currently a world-wide concern. Hence, the development of new therapies in order to eliminate strains of multiresistant microorganisms is mandatory. In this context the use of nanomaterials with antibiotic activity has become recognized such as silver nanoparticles (AgNP), which are able to inactivate different strains of microorganisms, mainly due to the delivery of Ag^+ as microbicide [1]. Additionally, hybrid nanomaterials based on the conjugation of AgNP with biomolecules are also used for antibiotic purposes [2]. Therefore, in this report we evaluated a possible synergistic antibacterial effect of hybrid AgNP stabilized with lysozyme (AgNP@LZ), a protein with lytic activity on the cell wall of some Gram positive bacteria, and comparing with those stabilized with citrate ion (AgNP@CIT), by incubation of pathogen microorganisms under both blue-light illumination and dark conditions. The *in situ* preparation of both AgNP in the presence of LZ or CIT was performed by UVB photo-cleavage of Igarcure-2959 and subsequent ketil radical reduction of Ag^+ [3], and the formation of the AgNP was monitored following the growth of the surface resonance plasmon absorbance with maximum around 400 nm.

The determination of the Minimum Inhibitory Concentration (MIC) of both nanomaterials was evaluated on 4 strains of clinical interest: *Escherichia coli* (*E.coli*), *Klebsiella pneumoniae* (*K. pneumoniae*), *Serratia marcescens* (*S. marcenscens*) and *Staphylococcus aureus* (*St.aureus*) in Muller Hinton agar and broth medium. AgNP@LZ did not show antimicrobial effect, opposite to the case of AgNP@CIT and control tests of LZ and Ag^+. This striking result led us to explore the reasons of the loss of antimicrobial effect of AgNP@LZ. Binding studies by stationary absorbance and fluorescence spectroscopies indicated the formation of a LZ/Ag^+ aggregates, while combined ATR-FTIR, circular dichroism, and fluorescence studies demonstrated that the covering of AgNP with LZ produces the loss α-helix conformation of the protein [4] together with oxidation of Trp residues, e.g., W62, and consequent loss of its lytic activity. Additionally, the tightly protein shell formed on the surface of AgNP prevents or strongly reduces the delivery of Ag^+ to the solution and prevents a microbicidal activity [5].

Thus, the photoreduction of Ag^+ in the presence LZ produces a very stable hybrid AgNP@LZ without antimicrobial activity.

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P87- Sensitized photooxidation of gamma-terpinene by Vitamin B2

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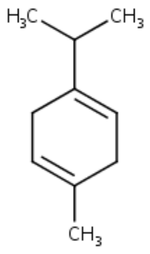

Fig. 1. γ-terpinene (γ-ter)

Flavoring and flavoring agents (Ars) are frequently used as food additives because of their ability to improve organoleptic properties and even enhance flavors. Another important characteristic of the Ars is given by their ability to act as antimicrobial agents by increasing the preservability of food [1]. In particular, γ-terpinene (γ-ter, Figure 1) is a volatile essential oil with antimicrobial properties, antioxidant and anti-inflammatory activities. It is used in food as an ingredient, in the production of peppermint and lemon essential oil, in the production of pharmaceutical drugs, and even in perfumes.

On these bases, it is interesting to know the photostability of Ars that, in the event of light induced reactions, can be transformed and fail to meet or modify the specific functions for which they were employed.

We carried out a kinetic and mechanistic study about sensitized photooxidation of γ-ter with Riboflavin (Rf), a natural sensitizer that is a common ingredient in a great variety of foods.

Preliminary assays on the visible light-irradiation of Rf + γ-ter showed that the substrate is degraded by the reaction with either electronically excited states of Rf or reactive oxygen species (ROS), the latter generated from the triplet excited state of the Rf (^{3}Rf*). The interaction between electronic singlet excited states of (^{1}Rf*) and ^{3}Rf* with γ-ter were studied by fluorescence and laser flash photolysis. Rate constant values of 2.18×10^9 $M^{-1}s^{-1}$ and 2.36×10^8 $M^{-1}s^{-1}$ were determined for the overall interaction of γ-ter with ^{1}Rf* and ^{3}Rf* respectively.

Rose Bengal was used as sensitizer to study the participation of singlet oxygen ($O_2(^1\Delta_g)$) in the degradation of γ-ter. Time-resolved phosporescence of $O_2(^1\Delta_g)$ and O_2 uptake do not show any type of interaction between $O_2(^1\Delta_g)$ and γ-ter.

In order to verify the participation of the other ROS sensitized by Rf, experiments of oxygen and substrate consumption were made in the presence of specific inhibitors for different ROS. Only in the case of catalase significant changes were observed evidencing the participation of H_2O_2 in the degradation of γ-ter .

Under aerobic sensitizing conditions the γ-ter oxidation is possible by either reaction with ^{3}Rf* or with H_2O_2, and this process could modify flavour and other properties of the compound.

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P88- Insights into the mechanism of light and temperature perception through BlsA in *Acinetobacter baumannii*.

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The ability of *Acinetobacter baumannii* to move is considered a pathogenicity factor given that it could contribute to bacterial persistence and dissemination in the nosocomial setting, in addition to biofilm formation and bacterial resistance to antimicrobial compounds. We have demonstrated that motility is modulated by light at 24ºC in this microorganism [1], resulting in inhibition of motility under blue light while the bacteria move throughout the plate in the dark. This bacterial response depends on the expression of the blue-light-sensing A (*blsA*) gene, which codes for a photoreceptor protein that contains an N-terminal blue-light-sensing-using flavin (BLUF) domain. Hence, the *blsA* transcript and protein levels were lower at 37°C than at 24°C in cells obtained from motility plates [1], with the concomitant lack of photoregulation at high temperatures. More recently, we extended the study of the BlsA photocycle as a function of temperature by spectroscopic characterization [2], demonstrating that between $15°\mathrm{C} < T < 25°\mathrm{C}$ the photoactivation to the signaling state sBlsA occurred with an average quantum yield of 0.20 ± 0.03, but it was practically inoperative at $T > 30°\mathrm{C}$, due to conformational changes produced in the nanocavity of FAD. This effect would be important when the photoreceptor is already present in the cell to avoid almost instantaneously further signaling process when it is no longer necessary, for example under circumstances of temperature changes possibly faced by the bacteria, allowing us to propose a model of integration of both light and temperature signals through BlsA [2].

To broaden our knowledge on the mechanism of signal perception and transduction in *A. baumannii*, in this work we have focused on the characterization of the transition from the photoregulation-proficient to the light-insensitive states observed in this organism, mediated by BlsA. Our results using strain ATCC 17978 show that the critical temperature for motility photoregulation is 24 (±0.06) ºC. In particular, we observe inhibition of motility at 23 and 24ºC under blue light, while the bacteria are able to move from 25 until 37ºC under the same illumination conditions. We further characterized this effect by studying *blsA* transcript levels in cells obtained from motility plates at these temperatures through qRT-PCR and found that *blsA* levels are important for adaptation to temperature changes, in addition to other more instantaneous mechanisms such as control of BlsA photoactivity. When the photocycle of BlsA protein was characterized by static and dynamic fluorescence spectroscopy at temperatures ranging from 14 to 37 (±0.1) ºC, we found a loss of the photocycling ability around 24-25ºC, since above this temperature fluorescence data indicated a loosening of the nanocavity of FAD.

Hence, we demonstrate by the linking of physiological and biophysical data how evolution has chosen this combined light and temperature modulation to ensure the survival of this pathogen, also modulating global features related to persistence and virulence in the nosocomial pathogen *Acinetobacter baumannii.* Getting insights into the mechanism of light perception and transduction could contribute to broaden our understanding of this important behavior.

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P89-Radiative energy transfer of Čerenkov light to a highly fluorescent ionic liquid

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Čerenkov light is produced when a charge particle moves in a dielectric medium faster than the light in that medium. This kind of radiacion is usually used to determine the activity of high energy beta emitters in a radioactive solutions. Acording to Tamm theory [1], the intensity of Čerenkov light decays as the wavelength increases, reaching the visible range only an small fraction. Since typical photomultipliers for liquid scintillation counting have a maximum response around 420 nm, the detection efficiency of Čerenkov radiation is usually low.

We have already shown [2] that a novel class of reusable solvent, the ionic liquid 1-Butyl-3-methylimidazolium Cloride (BMIMCl) (refraction index n ~1.5) is suitable to determine the specific activity of a ^{18}F solution (emitting positrons up to 634 keV) by means of Čerenkov counting with a detection efficiency of 6%.

In the present work, we evaluate the effect of adding a highly fluorescent ionic liquid to BMIMCl in order to shift the Čerenkov spectrum toward the red by means of radiative transfer. For this purpose, we synthesized the ionic liquid 1-Butyl-3-methylimidazolium 8-hydroxypyrene-1,3,6-trisulfonate (BMIMHPTS). A remarkable feature of this compound is that the absorption and the emission spectra correspond to the acidic species, since the ionic liquid enviroment is an extremely weak proton acceptor. These photopysic characteristics, along with an unitary fluorescence quantum yield, make the BMIMHPTS optimum to reabsorb the Čerenkov radiation in the UV region (low photocathode responsivity) and to re-emit it as fluorescence in the blue region (optimum photocathode responsivity).

We measured the Čerenkov spectrum with and without the addition of BMIMHPTS to BMIMCl, using a ^{32}P solution (emmiting electrons up to 1711 keV). In a home-made arrengement, seven cut-off filters were sequencially interposed between the sample an a Hamamatsu™ photomultiplier to recover the desirable spectrum. The reduction of the Čerenkov light at shorter wavelengths and the presence of fluorescence at higher wavelengths when BMIMHPTS is addeed, clearly indicate an energy transfer process. The low concentration of BMIMHPTS (3×10^{-4} M) points out to the radiative nature of this phenomenon.

Absorption and steady-state emission experiments in different BMIMHPTS/BMIMCl mixtures enables us to estimate the optimal concentration of pyranine yielding the highest fluorescence signal. Then, we perform several nuclear experiments looking for the optimal pyranine concentration in a TDCR system (Triple to Double Coincidence Ratio) composed of three photomultipliers arranged at 120 degrees [3]. We found that a concentration in the order of ~ 0.3 mM of BMIMHPTS in BMIMCl maximizes the overal detection efficiency. By Čerenkov counting, we were able to determine the activity of the ^{32}P solution with high accuracy (less than 2 % of relative error). We also show that the addition of BMIMHPTS increases the overall efficiency from 58 to 66 % for ^{32}P and from 6 to 13 % for ^{18}F.

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P90- Perovskite Photoluminescence quenching by electrogenerated donor and acceptor polymers.

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Solar cells based on hybrid organic-inorganic materials with perovskite crystallographic structure have attracted extensive attention that has exponentially grown since their first introduction in 2009 [1],[2]. A hot topic in this field is exploring inexpensive, stable and effective hole and electron transporting materials (HTMs and ETMs) in order to improve the device performance and to be favorable for large-scale production in the future. The HTMs and ETMs have been proven to be important components of perovskite solar cells, and they can form selective contact being favorable for reducing charge recombination and effective charge collection, thus resulting in the enhancement of power conversion efficiency. The use of metallic oxides such as TiO_2 and SnO_2 makes the solar cells production more expensive because of the use of high temperatures in the sintering process. Also, the HTMs and ETMs must face the problem of partial or complete dissolution by the organic solvents used in the posterior deposition of the perovskite layer. A possible solution to these problems is the use of HTMs and ETMs generated by electrochemical polymerization. The use of electrogenerated films has the advantage of being synthesized in one single step, which allows fine control over the film thickness and morphology, very important parameters when fabricating optoelectronic devices.

Porphyrins have been widely used as donor materials, interlayer or light-absorbing dyes in the field of organic photovoltaic and dye sensitized solar cells. On the other side, C_{60} fullerene is a strong electron acceptor that has proven to efficiently work in organic photovoltaic solar cells. Both, porphyrins and fullerene can be easily modified with electropolymerizable groups in order to obtain thin films over different substrates [3],[4].

In this work we present the formation of new films generated by electropolymerization of both, porphyrins and also fullerenes, for their utilization as HTM and ETM in perovskite based solar cells, respectively. The polymers were generated over conductive substrates by an electrochemical technique. SEM images showed that polymers completely cover the substrates, and that posterior deposition of the perovskite over the polymers results in the formation of very uniform perovskite layers.

Photoluminescence experiments showed that perovskite photoluminescence is quenched by the porphyrin and fullerene electropolymers. These results indicate that the porphyrin electropolymers can work as hole extraction and transport layer, while the fullerene works as electron transport and extraction layer.

The use of a simple electrochemical methodology in the formation of organic hole and electron transport layers in perovskite solar cells opens a new approach for the fabrication of efficient energy conversion systems.

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P91-Determination of the photosensitizer character of singlet molecular oxygen in the development of phototoxicity associated with the use of triamterene and its combination with hydrochlorothiazide

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Currently some families of drugs have been reported as photosensitive as a result of their interaction with electromagnetic radiation [1,2,3]. Within this group there is the triamterene (TAT), which is a diuretic of the family of aminopteridine whose action mechanism is a potassium sparing. TAT is a compound that absorbs in the UV region (Fig 1), exhibits a high fluorescence yield [2], and has been shown to degrade slowly under UVA irradiation [4].

Studies of photostability with UVB light (290-320 nm) in methanol, PBS and human serum albumin have reported photodegradation of TAT and the formation of products incluiding a dimer [5], which was not detected with UVA light (320-400 nm), in which the TAT has a significant absorption. In the presence of oxygen, the formation of singlet molecular oxygen $^1O_2(^1\Delta_g)$ was detected through the use of quenchers, such a L-histidine, dimethylfuran and furfuryl alcohol [2], indicating that this species can be responsible for the photoxicity of this drug [5]. Howevwe, the quantum yield for generation of singlet molecular oxygen (ϕ_Δ), has no ben reported.

We complement the study of TAT as a photosensitizer with formation $^1O_2(^1\Delta_g)$ and its phototoxicity with steady state and time resolved emission spectroscopy and detection of the triplet states of the compound. Moreover, this drug is used in combination with other active principles, such as hydrochlorothiazide (HCT). Therefore, we incorporate the study of the ϕ_Δ of TAT in the presence of HCT, evaluating the interactions of both compounds in terms of complex formation, performing absorption, fluorescence and kinetic decomposition studies.

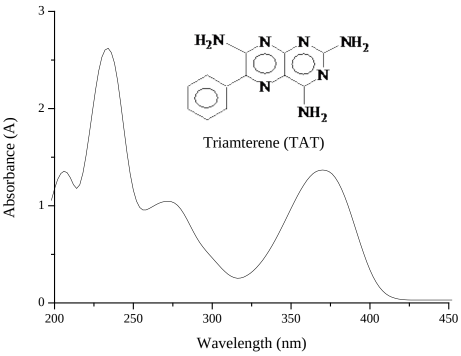

Fig 1. Ultraviolet absorption spectrum of an ethanol solution of triamterene (7.36 x10^{-5} M)

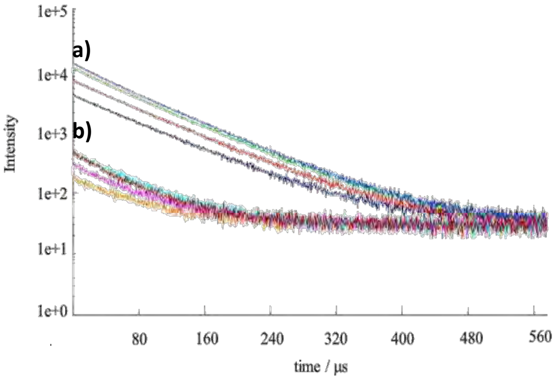

Fig 2. Phosforescence of $^1O_2(^1\Delta_g)$ generated by photosensitization of (a) PNF and (b) TAT in aereated acetonitrile solution.

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P92- Photocatalytic activity Composites of TiO_2-Graphene sensitized by *Bactris Guineensis*

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Heterogeneous photocatalysis is a promising alternative in degradation of recalcitrant compounds in wastewater and TiO_2 is the photocatalyst most investigated, despite to be photocatalytic active only under UV light [1]. Currently, several strategies are used for improving TiO_2 photocatalytic activity in a visible range (e.g., surface modification, quantum dots, noble metal deposition, coupled semiconductor, ion modification, doping and sensitization, etc.). Among this, natural dye sensitization is an inexpensive and non toxic alternative [2]. Furthermore, coupled semiconductor to other materials is a common strategy used to improves electric transportation inside a catalyst. We propose the sensitization of composites graphene-TiO_2 with a natural extract from a Caribbean Colombian tree named Corozo (*Bactris Guineensis)*. We extracted a dye from *Bactris Guineensis* by a percolation process. TiO_2 and TiO_2-Graphene thin films were deposited by doctor blade method and sensitization was carried out after chemisorption. Catalysts were characterized by Raman, XRD and diffusse reflectance assays. Finally we tested the photocatalytic properties for the photodegradation of methylene blue.

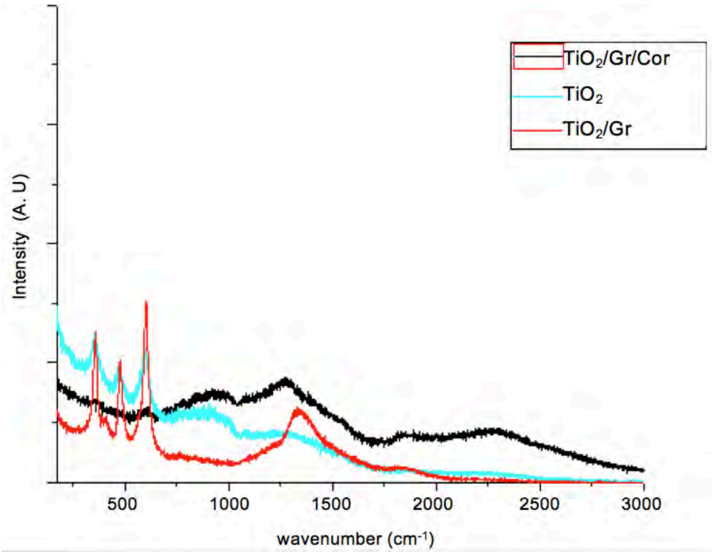

Fig.1. Raman Spectra of thin films of TiO_2, TiO_2/Gr and TiO_2/Gr/Cor thin films.

Fig 1 shows a Raman spectrum of thin films of TiO_2 (light blue), TiO_2/Gr (red) and TiO_2/Gr/Cor (black). Thin signals located at 398 cm^{-1}, 520 cm^{-1} and 639 cm^{-1} are associated with vibration (E_{1g}) of the TiO_2 anatase. Furthermore, TiO_2/Gr thin films show a broad signal located at 1340 cm^{-1}, this signal can be assigned to G vibration of graphene, associated with sp^3 bonds [3]. Furthermore, the TiO_2/Gr/Cor thin films show broad signals that overlap TiO_2 and graphene signals. Photocatalytic results indicated that TiO_2/Gr and TiO_2/Gr/Cor thin films were effective in degradation of methylene blue under visible irradiation.

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P93-Photodynamic treatment for microbiologically polluted water.

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The availability of clean water is one of the greatest challenges facing humanity today. Traditional methods of bacteriologically contaminated water purification are widely used as sodium hypochlorite, ozone, X radiation, etc. The use of these systems has negative aspects, such as induction of resistance due to its permanent use, especially in stored waters (ponds) for human or industrial use.

Photodynamic processes have been successfully used against infection and microbial contamination. Its advantages are a broad spectrum of action because photosensitization protocols affect Gram-positive and Gram-negative bacteria, as well as outside the classification of Gram (for example, mycoplasma), fungi, yeasts, protozoa, Parasites. Other advantages are great reduction of bacterial concentration, similar efficacy against wild and antibiotic resistant strains, absence of strains resistant to photodynamic action, and absence of mutagenic effects in bacteria. An interesting possibility is the use of sunlight for the activation of photosensitizers, with the comparative advantage of high solar radiation in the north of Chile.

In this study, we investigate the possibility of using flavins as photosensitizers for the disinfection of microbiologically polluted waters. Riboflavin (RF), the precursor of all flavins, is known as vitamin B_2 and it is essential for all aerobic organisms.

The first trials, using RF and light to disinfect water contaminated with the gram-negative bacterium *Escherichia coli*, did not give positive results. However, the effect of light and RF was that expected on the Gram-positive bacteria, *Bacillus cereus* and *Staphylococcus aureus*, with a considerable reduction on the bacterial load in the treated waters.

The low effect found on *E.coli* could be due to the very low incorporation of the dye into this Gram-negative bacterium. With the aim of increasing the photosensitizer incorporation into bacteria, we use the 1´2´3´4´-tetrabutyryl ester of RF (TRB).

The results indicate a significant decrease in the *E coli* content in waters treated with TRB and light. This effect was even greater on waters contaminated with *B.cereus* and *S.aureus.*

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P94- *In vitro* viral inactivation photosensitized by natural anthraquinones

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From the phototoxic plant, *Heterophyllaea pustulata* Hook. f. (Rubiaceae), a bush that grows in the Andean northwest of Argentina, we have obtained 9,10-anthraquinone derivatives (AQs) with photosensitizing properties [1-3]. Previously, we have demonstrated that these AQs show *in vitro* virucidal effect against Herpes Simplex virus Type 1 (HSV-1), which means an inactivation of viral particles before their entry into the host cells, and this inhibition was increased by light action (photostimulation) [4]. The aim of this work was to study the *in vitro* inactivation of HSV-1 once the virus entered into the host-cells, by the photosensitized action of two natural AQs: soranjidiol (Sor) and 5,5'-bisoranjidiol (Bisor), a soranjidiol dimer.

Isolated AQs were identified by their RMN spectra. To test the viral inactivation effect of each AQ on infected cells, it is previously necessary to find the concentrations of each AQ that are not toxic for the host cells (cytotoxic assay). In the two assays, morphological cellular alterations were evaluated by optical microscopy (cytopathic effect, CPE) and cellular viability (CV) was determined by uptake NR assay, under two simultaneous conditions: darkness and irradiation (actinic lamp 380-480 nm, Philips TL/03). Cytotoxic test was performed in a monolayer of Vero cells (host cells) treated with different concentrations of each AQ, dissolved in MEM with DMSO <1%. Non cytotoxic concentrations were estimated from a dose-response curve (% CV *vs.* concentrations) [5]. Thus, a Subtoxic Concentration (SubTC, CC_{20} concentration that ensures 80 % of viable cells) and the Maximum Non-Cytotoxic Concentration (MNCC, CC_{10}) were established. Subsequently, infected cells with HSV-1 (KOS strain) were incubated 4 h with each AQs at SubTC and MNCC, and then irradiated for 15 min. Active viral particles after both treatments (darkness and irradiation) were detected by extraction of cellular content and its subsequent inoculation in a new Vero cell monolayer to evaluate by Plaque reduction assay after 72 h of incubation [6]. Cellular, viral, toxicity and positive (Acyclovir) controls were included. The inactivation results were expressed as percentage of plaque inhibition (%I) by comparison with viral controls.

Bisor was more toxic than Sor, and the toxicity was increased by the irradiation. For Sor the SubTC was 393μM and the MNCC was 137μM, whereas for Bisor they were 79μM and 59μM, respectively. In darkness, the virus was not inactivated by any AQ, but a significant inactivation was observed under irradiation. Sor inactivated 95% and 57% of viral particles at SubTC and MNCC respectively. On the other hand, Bisor inactivate 38% only at SubTC. The cellular controls show that the irradiation not produces significant changes in the cell control, viral control and the toxicity controls had the same effects which were observed in the cytotoxicity assay.

In conclusion, Sor was better than its dimer Bisor, since it photo-inactivated 95% of HSV-1 particles and also it is less cytotoxic. This result motivates us to continue to deepen studies with purified AQs, with the aim to provide a basis for the development of new treatments for viral etiology lesions.

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P95- Photophysical Characterization of Phenalenone Derivatives

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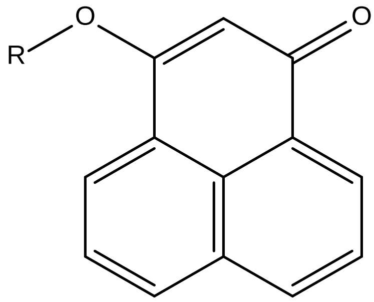
Phenalenone has been studied extensively due to its behavior and because it can be used on interesting applications from the scientific and technological point of view. We are interested in obtaining and characterizing phenalenone derivatives able to interact with specific targets, like lectins, and generate singlet oxygen promoting damage at specific selected locations. 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 position 3 of the phenalenone ring, we prepared and studied the derivatives shown.



R= H
Et
$(CH_2)_6OH$
$(CH_2)_9OH$
$(CH_2)_6$OMannoside
$(CH_2)_9$OMannoside

When compared with phenalenone, the capability of the different compounds to generate singlet oxygen is reduced, for example, in acetonitrile 3-hydroxy-phenalenone has Φ_Δ equal to 0.8, while for all other derivatives the quantum yield is lowered to 0.6. Additionally, singlet oxygen quenching is observed. All derivatives showed a low emission quantum yields, for 3-hydroxy-phenalenone a dual emission was observed, which can be related to the equilibria between diketo and enol tautomers, which is not observed for the other compounds.

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P96- Photochemical Behaviour and Potential Antibacterial Properties of Rhenium Complexes Bearing P,N-Bidentate Ligands

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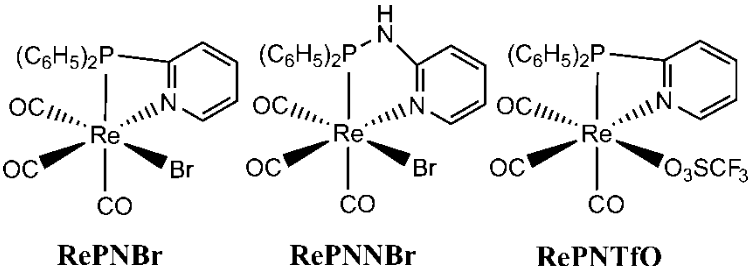
Rhenium (I) tricarbonyl complexes present remarkable luminescent properties that have attracted much attention in last decades. The convenient and easy synthesis and later the possibility to rationally change the ligands, have allowed the development of a wide range of interesting and important applications, including their use as catalysts, molecular probes, light-emitting materials, nonlinear optical materials, binding or photocleavage of DNA, and radiopharmaceuticals.
In this work, we present the photochemistry of different mononuclear complexes like [*P,N*-$\{(C_6H_5)_2(C_5H_4N)P\}Re(CO)_3Br$] (**RePNBr**), [*P,N*-$\{(C_6H_5)_2(C_5H_4N)P\}Re(CO)_3(O\text{-}CF_3SO_3)$] (**RePNTfO**) and [*P,N*-$\{(C_6H_5)_2(C_5H_4N)NHP\}Re(CO)_3Br$] (**RePNNBr**) (Scheme 1) which has been characterized as a dual emitter.[1,2] The absorption and emission properties of these complexes have been evaluated using steady state and time resolved techniques. Thermal stability, photochemical behaviour, luminescence lifetimes and quantum yields of singlet oxygen generation are reported and discussed, and also potential antibacterial properties have been evaluated in strains of Escherichia coli and Staphylococcus aureus.



Scheme 1. Structural diagram of [*P,N*-$\{(C_6H_5)_2(C_5H_4N)P\}Re(CO)_3Br$] (**RePNBr**) and their parent complexes [*P,N*-$\{(C_6H_5)_2(C_5H_4N)NHP\}Re(CO)_3Br$] (**RePNNBr**) and [*P,N*-$\{(C_6H_5)_2(C_5H_4N)P\}Re(CO)_3(O\text{-}CF_3SO_3)$] (**RePNTfO**)

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P97-Organic Light-emitting Diodes based on PVK and Zn(II)Salicylidene Composites

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There is global interest in the development of environmentally friendly materials for applications in opto-electronic devices, including light-emitting diodes, operating with high efficiency, easy processability and low environmental impact.[1] Light-emitting diodes are one particular type of potential device, in particular those fabricated using organic materials, the organic light-emitting diodes (OLEDs), which can be more easily processed and recycled than the inorganic-based conventional systems.[2]–[4] Thus, in this study the photo- and electroluminescence properties of OLEDs processed by spin-coating composed of composites formed with PVK and two Zn(II)salicylidenes were studied (Figure 1). Our results showed that the optical-electronic properties of the OLEDs were greater for the Zn(II) compounds than for the free ligands. This study has shown that PVK and organic molecules or coordination compounds are suitable systems for solution-processable diodes by a single spin-coating step deposition. The addition of the benzophenone moiety on [Zn(salophen)] structure improves its optical properties in solutions as well as in solid-state. Additionally, the FRET process observed in the PL might quench the donor excitons, but in the case of PVK, the most important parameter for the absence of the EL emission is probably the lower efficiency of the exciton formation in the diodes. The free ligands presented poorer EL efficiencies than the Zn(II) coordination compounds, [Zn(salophen)] and [Zn(sal-3,4-ben)], showing that the metallic ion plays an important role in the charge transport properties and its phenomena was proven by the hole mobility obtained from JxV power law ($\mu_{Zn(salicylidenes)} > \mu_{salicylidenes}$). Also, this is the first time that hole mobility were correlated with molecular structure for solution-processable salicylidene based devices in the attempt to tune optical-electronic properties. We also have shown that coordination compounds of metals with greater natural abundances might be explored as materials for light-emitting diodes.

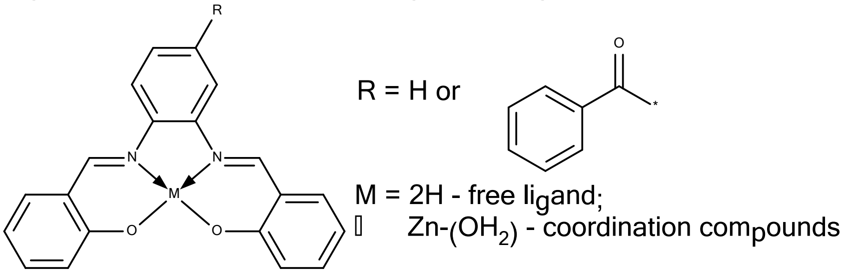

Figure 1. Molecular structures of salicylidene derivatives

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P98-Effects of constant exposure to LED lights in different populations of retinal neurons.

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The retina is a complex neural circuit that transduces light into a pattern of electrical impulses to the brain. This tissue fulfills a visual role through rods and cones and the synchronization of circadian rhythms through ganglion cells (GCs), specifically through a subpopulation of photosensitive GC (ipRCGs) [1]. Epidemiologic studies and numerous case reports demonstrate that light can indeed injure the human retina [2]. Light damage and retinal degenerative diseases in humans and animal models have an important feature in common: cell loss by apoptosis of photoreceptors and pigment epithelium cells (PE). This crucial feature may render light damage a suitable model system to investigate cellular and molecular mechanisms of cell death. The process of retinal degeneration (RD) produced by low-intensity light stress has not been well-characterized yet [3]. To understand the mechanism of retinal damage by light and assess the biochemical changes taking place, we studied in Wistar rats the effects of constant exposure for different times (1 to 8 days) to LED sources at low 200 lux. We demonstrate that photoreceptor cells die after five days of light exposure with a reduced functionality of these cells after 4 days of light exposure. The mechanism of cell death could be attributed to the constant activation of phototransduction and oxidative stress [3].

In the present work we proposed to continue evaluating the constant low LED light stimuli effects over visual and non-visual photoreceptors. We study Rhodopsin (Rho), Melanopsin (Opn4) and Neuropsin (Opn5) expression and Rho phosphorylation. Male Albino *Wistar* rats were exposed to white LED light (200 lx) for 1 to 8 days and the retinas were processed for histological, proteins expression and localization analysis. We found that the number of GCs was not altered by light exposure. The expression of Opn4 increased and its location varied from neurites to somas along the days. Opn5 was localized in GCs and inner nuclear layer with higher expression levels after 6 days. Also, we found that Rho phosphorylation was reversible if the animals were exposed to 48 hours of darkness after light treatment.

Our results demonstrated that, constant light produces a specific retinal remodeling within the outer retina with a significant cell death in the ONL as previously reported; by contrast, in the inner retina and cells located at the INL and GCL, continuous light exposure does not affect cell survival while a substantial relocation of nonvisual photopigments OPN4 and OPN5 responsible for sensing light in the inner retina, could be easily observed.

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P99- Gas-phase and matrix-isolation photochemical studies of diallyl sulfide

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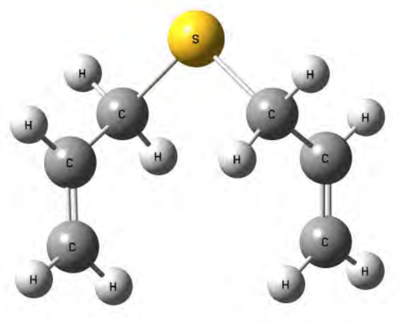
In this work the photochemistry of diallyl sulfide (DAS) in presence of molecular oxygen was studied either in gas phase or in matrix isolation conditions at cryogenic temperatures by means of FTIR spectroscopy. This study is part of a general proyect aimed at the investigation of the photochemistry of organosulfur volatile compounds presenting atmospheric interest [1,2]. Dially sulfide, $CH_2{=}CH{-}CH_2{-}S{-}CH_2{-}CH{=}CH_2$, is one of the main constituents of garlic. Its presence in the atmosphere was repoted, and attributed to different sources ranging from natural to industrial processes [3].



Structure of dially sulfide

As might be expected from its UV-visible spectrum in gas-phase, DAS is stable under UV-visible light (800-200 nm). Gaseous mixtures of DAS and O_2 in different proportions were exposed to light from a Hg-Xe lamp, and the evolution of the photoproducts were followed by FTIR spectroscopy. Inittially, acrolein ($CH_2{=}CH{-}C({=}O)H$) and sulfur dioxide (SO_2) were produced. Carbon dioxide (CO_2), carbon monoxide (CO) and carbonyl sulfide (OCS) were also detected. Acrolein was an intermediate in the reaction, giving formic acid (HCOOH) at longer irradiation times. When the wavelength of the light was limited to the 450 to 350 nm range, formic acid was not produced, and acrolein, togheter with the other photoproducts, remained as stable products.

The photochemical reaction of DAS and O_2 was also studied in matrix conditions. The matrix isolation technique combined with FTIR spectroscopy was specially well suited for the study of reactive species, van der Waals complexes, free radiacal and intermediate species. Mixtures of DAS:O_2:Ar in different proportions were deposited onto a cold CsI window (~10 K) using the pulsed depositions technique. The high dilution of the reactant mixtures with respect to the inert gas prevents any other mechanisms than bimolecular ones. The integrated intensities of the IR signals were plotted against the irradiation time, and subsequently grouped according to their kinetic behavior. The photochemical mechanisms were proposed, based on the detection of the intermediates and final products.

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