

XII ELAFOT

2015, Maresias - SP, Brazil



**XII ENCONTRO LATINO-AMERICANO DE
FOTOQUÍMICA E FOTOBIOLOGIA**

**XII LATIN-AMERICAN MEETING ON
PHOTOCHEMISTRY AND PHOTOBIOLOGY**

April 26 – 30, 2015

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Preface

Dear Colleagues and Friends

We are delighted to welcome you to the *XII Encontro Latino Americano de Fotoquímica de Fotobiologia*, held in the captivating seaside village of Maresias on the coast of São Paulo State from April 26 – 30, 2015. Elafot is an international meeting with a long-standing tradition in Photochemistry and Photobiology in Latin America and it brings together Latin American Scientists and renowned invited speakers from all over the world. In its XII Edition, papers on basic and applied Photosciences covering critically important themes, including photocatalysis, advanced light spectroscopy and microscopy, single molecule photochemistry, luminescent nanoparticles and polymers, photodynamic therapy, sustainable photo technologies and other related fields will be presented in six Plenary Lectures, twelve Invited Lectures, two Techno-Scientific Lectures and ten Oral Communications besides two poster sessions with more than sixty contributions. The XII Elafot Edition has opened a new issue with the elaboration of a permanent website www.elafot.org that will help organization in future editions keeping memory and information of late events.

We wish you a stimulating meeting and a pleasant stay in Maresias!!!

Organizing Committee

PL: Plenary Lecture (45 + 5 min); INV: Invited Lecture (35 + 5 min); TEC: Techno-Scientific Lecture (30 + 5 min);

OC: Oral Communication (15 + 5 min) FT: Flash Talk (5 minutes each).

	Sunday 26	Monday 27	Tuesday 28	Wednesday 29	Thursday 30
8:10 – 8:30		Opening			
8:30 – 9:20		PL1 David Whitten	PL3 Johan Hofkens	PL5 Markus Sauer	
9:20 – 10:00		INV1 Cornelia Bohne	INV5 Rodrigo Palacios	INV8 Cleber Mendonça	INV11 Antonio Tedesco
10:00 – 10:20		OC1 Miguel Gervaldó	OC4 Hans Waldenmaier	OC7 Beatriz Barja	OC10 Bernardc De Souza
10:20 – 10:40		Coffee Break	Coffee Break	Coffee Break	Coffee Break
10:40 – 11:20		INV2 Claudio Borsarelli	INV6 Fabiano Rodembusch	INV9 Kris Janssen	INV12 Carolina Aliaga
11:20 – 11:40		OC2 Mariana Vignoni	OC5 Laura Raurell	OC8 Diego Lencione	Closing
12:00 – 15:00		Lunch time	Lunch time	Lunch time	
15:00 – 15:50	Registration	PL2 Malcolm Forbes	PL4 João Carlos Lima	PL6 Daniel Martire	
15:50 – 16:10	Registration	OC3 Gabriela Bosio	OC6 Reinaldo Rodrigues	OC9 Pedro Aramendia	
16:10 – 16:50	Registration	INV3 Marcelo Ganzarolli	INV7 Germán Günther	INV10 Alexis Aspée	
16:50 – 17:20	Registration	Coffee Break	Coffee Break	Coffee Break	
17:20 – 18:00		INV4 Denis Funtealba	TEC1 João Lucas Rangel	TEC2 Ian Stanton	
18:00 – 18:20		FT1 - FT4	FT5 - FT8		
18:30 – 19:30	Welcome	POSTER	POSTER		
20:00	Reception				BANQUET

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PLENARY LECTURES

PL1 – PL6

PL1

Photochemistry and photophysics of oligo-phenylene ethynyls and their complexes with surfactants

David G. Whitten

Center for Biomedical Engineering University of New Mexico

This presentation will begin with an introduction of the antimicrobial activity of Oligo- and Poly-Phenylene Ethynylene polyelectrolytes and then focus on their photochemical and photophysical properties and their abilities to form complexes with detergents above and below their critical micelle concentrations and with other amphiphilic molecules. We will discuss how these properties lead to their potential applications of sensing and selective destruction of proteins and pathogens.

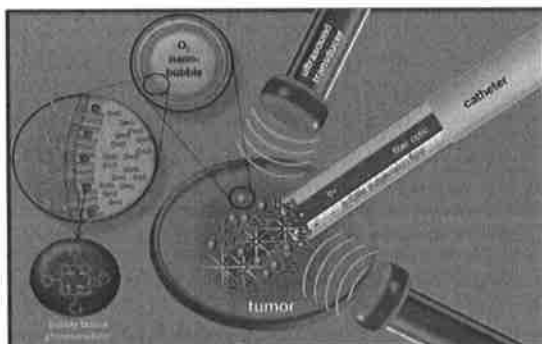
PL2

Photodynamic therapy, toils and troubles: problems solved with tiny bubbles

Malcolm D.E. Forbes

Department of Chemistry University of North Carolina Chapel Hill, NC 27599

Photodynamic therapy (PDT) uses visible light, a sensitizer such as a porphyrin, and oxygen gas to create singlet oxygen ($^1\text{O}_2$), a reactive oxygen species that can kill cancer cells. Historically, PDT has remained a non-invasive treatment, using red light and ambient oxygen after intravenous administration of the sensitizer. Here we describe an invasive methodology for PDT that uses highly efficient blue light coupled with localized microbubble-based delivery of sensitizer and oxygen. Lipid-based air bubbles with stabilizers are administered via a teflon or stainless steel catheter containing a concentrically placed fiber-optic cable. Ultrasound transducers are used to acoustically image the catheter and bubbles. Ultrasound can also be used to manipulate the bubbles (moving or popping). The kinetics and topology of singlet oxygen production can be studied quantitatively by reacting secondary amines with the $^1\text{O}_2$ to produce stable nitroxide radicals, detectable at μM concentrations by electron paramagnetic resonance (EPR) spectroscopy. The sensitivity of nitroxide EPR spectra to local order in heterogeneous structures such as bubbles, vesicles, and micelles will also be presented and discussed.



In situ monitoring of catalysis at the nanoscale

Johan Hofkens

Katholieke Universiteit Leuven, Belgium

In situ characterization techniques directly relate the physicochemical properties of a catalyst to its catalytic activity, allowing a more rational catalyst design. As a result of the sensitivity and limitations of each spectroscopic approach, several problems are still unaccounted for (e.g. pressure gap, materials gap and phase gap). These shortcomings can be solved by applying new spectroscopic techniques. Our group has introduced fluorescence microscopy as a sensitive tool to monitor chemical reactions inside zeolite crystals; this directly reveals their catalytic activity and allows locating active zones with submicrometer accuracy, single molecule sensitivity and in three dimensions throughout individual catalysts crystal. Furthermore the scope of this technique extended by using specific probes, that target certain regions inside the catalyst particle. This site specific staining allows a 3D visualization of the particles properties. We have recorded nanoscale reactivity maps of working catalysts under in situ conditions by localizing single fluorescent reaction products. This is the first approach that allows quantification of the reactivity of catalytic nanodomains. Correlation of these fluorescence nanoscopic reactivity measurements with advanced electron microscopy data will help in rational design of improved catalysts for greening chemistry. This new form microscopy tailored for catalysis is coined NASCA. Mass transfer phenomena are known to play a crucial role in porous heterogeneous catalysts. When intraparticle diffusion is too slow to provide a sufficient flux of reactants to the inner parts of the catalyst particles, substrate depletion occurs and only the outer parts of the particles are efficiently used for catalysis. Quantifying the degree of intraparticle diffusion limitation by means of the Thiele modulus and the related effectiveness factor remains a big challenge. Only few techniques have the necessary spatial resolution and sensitivity to measure in situ the concentration profiles of products and/or reagents inside the catalytic particles. In this contribution it will be shown how fluorescence microscopy can be used to tackle this problem. The epoxidation of bulky substrates over mesoporous Ti-MCM-41 was chosen as a model case. It is shown how individual reaction events inside the Ti-MCM-41 particles are visualized and localized and how the obtained reactivity maps yield direct information on the Thiele modulus and effectiveness factor of this specific intraparticle diffusion limited catalytic process. Moreover, a value for the intraparticle diffusion constant and the intrinsic rate constant of the catalytic reaction could be estimated based on the data obtained by one in situ experiment. The presented

method is versatile and applicable to a variety of catalytic systems, provided that a suitable fluorogenic probe molecule is used, which preferably is detectable at the single molecule level after catalytic conversion.

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Multiplexing light outputs.inputs in nucleic acid sensors and actuators

João Carlos Lima

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The challenge of monitoring and controlling multiple events occurring simultaneously asks for the use of multiple fluorophores that can be individually addressed for probing or triggering a particular event. This is a difficult task due to the complexity of the overlapping signals, moreover organic fluorophores have usually broad absorption and emission bands, which limits the number of markers that can be successfully used in the visible spectrum.[1-3] We have previously reported the use of caged nucleotides for controlled polymerization of nucleic acids.[4] The system is based on ATP caged with [7-(N,N-diethylamino)coumarin-4-yl]methyl (DEACM), which can be released by light irradiation, thus allowing for the controlled triggering of in vitro RNA polymerization. We took one step further and introduced GTP caged with (7-methoxycoumarin-4-yl)methyl (MCM) for the development of a dual color setup that allows for the control of insertion of either one or the other nucleotide: release of either ATP or GTP (or both simultaneously) is attained via irradiation using a monochromatic light pulse.[5] A molecular beacon (MB) detects the formation of the RNA product. Light inputs are used to change the status of the system and select a population able to produce a sensing response to the presence of ATP or GTP.

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Localization microscopy by dstorm: from concepts to biological impact

Markus Sauer

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Through constant improvements in fluorescent probes, efficient and specific labeling techniques as well as refined data analysis and interpretation strategies single-molecule localization microscopy allows us today to interrogate how the distribution and stoichiometry of interacting proteins in subcellular compartments and molecular machines accomplishes complex interconnected cellular processes. Among all powerful high-resolution imaging techniques introduced in recent years localization microscopy excels at it delivers single-molecule information about the distribution and, adequate controls presupposed, even absolute numbers of proteins present in subcellular compartments. This provides insights into biological systems at a level we are used to think about and model biological interactions.

With a special focus on direct stochastic optical reconstruction microscopy (dSTORM), I summarize recent key developments and application examples of two-dimensional and three-dimensional (3D) wide-field and single-plane illumination localization microscopy with standard organic fluorophores. Furthermore, I will demonstrate correlative super-resolution fluorescence localization and scanning electron microscopy to map the position of proteins of nuclear pore complexes in isolated *Xenopus laevis* oocyte nuclear envelopes with molecular resolution in both imaging modes. The correlative images demonstrate quantitative molecular labeling and localization of nuclear pore complex proteins by standard immunocytochemistry with primary and secondary antibodies. In addition, I will demonstrate how localization microscopy can be used successfully to unravel the 3D molecular architecture of multiprotein complexes, e.g. the synaptonemal complex, with isotropic resolution.

The use of silica and magnetite nanoparticles in photochemical studies of environmental interest

Daniel Mártire

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CCT-La Plata-CONICET, Universidad Nacional de La Plata, La Plata, Argentina

Some organic contaminants dissolved in natural waters tend to adsorb on suspended particles and sediments. In order to mimic the photodegradation routes in natural waters of the phenolic contaminants Bromoxynil (herbicide) and Dichlorophen (anthelmintic and pesticide) adsorbed on silica, we prepared silica nanoparticles modified with these compounds. The particles were characterized by Fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) analysis, thermogravimetry (TG), dynamic light scattering (DLS), and UV-vis spectroscopy. The photolysis of aqueous suspensions of the nanoparticles was investigated in the absence and presence of the sensitizer Riboflavin. Immobilization on the particles influences the photolysis mechanism. The results also indicate that immobilization lowers the rate of collisional encounter, which affects the quenching rate constants for the reactions of excited triplet states and singlet oxygen with the contaminants. Kinetic computer simulations of the photodegradation routes of the contaminants in natural environments show that the relevance of the direct and indirect (through reactions with reactive species generated in photoinduced processes) photodegradation routes of the organic compounds are very much affected by sorption on silica.

On the other hand, the development of novel and cost-effective magnetic nanomaterials for environmental remediation has recently attracted considerable attention. In this context, we prepared and characterized magnetite nanoparticles coated with humic and fulvic acids. UV-A irradiation of suspensions of humic acids-coated magnetite nanoparticles under aerobic conditions was employed to degrade the emerging contaminant carbamazepin (psychiatric drug). The reduction of HgCl_2 to the insoluble product Hg_2Cl_2 photosensitized by fulvic acid-coated magnetite nanoparticles under anaerobic conditions and in the presence of formate is also discussed. Under these conditions the reducing radical $\text{CO}_2\cdot^-$ is formed.



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INVITED LECTURES

INV1 – INV12

INV1

Dynamics of cucurbit[7]uril binding to a guest with ground- and excited-state pKa shifts

Suma S Thoma, Cornelia Bohne *

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The 2-ammoniumanthracene cation (AAH⁺) undergoes deprotonation in the excited state and at low pH most of the emission occurs from excited AA at 503 nm. Cucurbit[7]uril (CB[7]) was previously shown to complex AAH⁺ leading to an enhancement of the emission from this species at 422 nm (Macartney et al. (2005) Chem. Commun. 5867-5869). The current work focuses on the kinetics of AAH⁺ complexation with CB[7]. Binding isotherms were determined using fluorescence. The equilibrium constant for the formation of the 1:1 complex at pH 2, where in the ground state AAH⁺ is fully protonated, was determined to be $4.8 \times 10^5 \text{ M}^{-1}$ ([NaCl] = 20 mM for all experiments). Time-resolved fluorescence studies showed the lifetime of AAH⁺ in the complex was lengthened to 8 ns. The excited state dynamics of the AAH⁺/AA system is completed with 0.5 μs and is much faster than the formation of the complex between AAH⁺ and CB[7] studied by stopped flow, where the kinetics took 0.2 s to reach equilibrium. The association and dissociation rate constants recovered from kinetic experiments were $4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and 10.8 s^{-1} , leading to an equilibrium constant of $4.1 \times 10^5 \text{ M}^{-1}$. This value is in good agreement with the binding isotherm studies. However, the continuous excitation of the solution to monitor the fluorescence from AAH⁺ in the stopped flow experiments led to the continuous formation of AA even at low pH. This effect led to the observation of a fast component close to the time resolution of the stopped flow experiment due to the binding of AA with CB[7]. Studies are currently underway at higher pHs to determine the impact of the presence of AA on the dynamics of this host-guest system.

INV2

Photosensitized protein modification: some biological and technological applications

Claudio D Borsarelli

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Photosensitized processes that involve either charge-transfer (Type I) or energy-transfer (Type II) are of major interest in biological and biotechnological fields. In this presentation we explored the modification of several proteins or enzymes (e.g. albumins, lysozyme, synuclein, lipase, etc.) by light-induced reactions using organic and inorganic sensitizers molecules. The results are discussed in terms of the effect of the protein milieu on the molecular distribution and photophysical properties of the sensitizer, protein oxidation and crosslinking effects, etc. Examples of biological activity and toxicity, and technological applications for the photosensitized modified proteins are presented.

INV3

Spotlight on topical nitric oxide-releasing biomaterials

Marcelo Ganzarolli de Oliveira

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A growing body of evidence shows that endogenous nitric oxide (NO) plays several physiological and pathophysiological actions in the skin. These include the proliferation and differentiation of epidermal cells and inflammatory responses that, in turn, affect the wound healing processes. More recently, it was shown that NO is also involved in (UV) radiation-induced melanogenesis and erythema/edema formation. These findings have prompted the development of several types of biomaterials capable of releasing NO topically. The potential uses of these materials include the treatment of peripheral vascular diseases associated with endogenous NO depletion, such as chronic leg ulcers and the vasoconstriction of Raynaud's syndrome. However, most of these materials face difficulties associated with lack of specificity and adequate control of the rate and the dose of NO release. In this scenario, the use of light has emerged as one of the promising strategies to modulate the delivery of NO locally from photolabile NO-releasing molecules. In this lecture, I will present an overview of previous and ongoing studies in my laboratory developing new platforms for the photochemical release of NO by visible light. These include functionalized hydrophilic and hydrophobic polymeric films and membranes and micellar hydrogels. I will describe special techniques that we have been using such as real-time chemiluminescence detection of photochemical NO release and laser Doppler flowmetry for measuring the potentiation of dermal vasodilation upon irradiation of topically applied NO-releasing films.

Drug-cucurbit[n]uril-protein biosupramolecular assemblies: improving drug photoactivity

Karina Scholtbach ¹, Ítalo Venegas ¹, Anita Tapia ¹, Hery Chung ¹, Javiera Cáceres ¹, Cornelia Bohne ², Denis Fuentealba ^{1*}

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Cucurbit[n]urils (CB[n], n = 5-10) are a family of macrocycles [1-2] that shows exceptional binding properties for biological applications. For the last couple of years, we have been working on using fluorescent methods to detect drug-CB[n]-protein ternary complexes and further exploring the photoactivity of the complexes. We believe combining the encapsulation properties of CB[n]s and the interaction of drugs with proteins will lead to the generation of novel drug transport systems with improved properties. Previous literature reports showed the formation of ternary protein assemblies [3-4]. We used time-resolved fluorescence lifetime and anisotropy to characterize the formation of such complexes with acridine orange (AO⁺), CB[7] or CB[8] and human serum albumin (HSA). We identified a ternary protein assembly only in the case of the CB[7] complex, while the CB[8] complex did not interact with the protein [5]. Other drugs such as methylene blue did not form ternary complexes in spite of forming tight complexes with CB[n], which suggested that drug protrusion out of the CB[n] cavity is a key feature in forming such assemblies. Irradiation of the AO⁺-CB[7]-HSA complex with visible light induced singlet oxygen and peroxides formation. Mechanistic studies using specific quenchers showed that the photosensitizing activity of AO⁺ in the ternary assembly was mainly through electron-transfer. In the absence of the protein, singlet oxygen quantum yield was significantly increased inside the CB[7] complex. Protein hydroperoxide generation was important compared to hydrogen peroxide. Protein oxidation and fragmentation were enhanced compared to the drug in the absence of CB[n]. Similar results were obtained with another ternary complex formed by a cationic porphyrin. Interestingly, the results were the opposite with methylene blue, which does not form a ternary complex with HSA, suggesting that the close proximity of the drug and the protein in the ternary complex favors photo-oxidation.

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INV5

Conjugated polymer nanoparticles as photosensitizers in aqueous media

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Conjugated polymer nanoparticles (NPs) have recently emerged as a new type of nano-materials of with interesting optoelectronic properties and potential application in organic opto-electronic devices such as solar cells, photo-catalyst and photo-sensors, etc. In this talk I will describe recent experiments on the synthesis and characterization of conjugated polymer nanoparticles and its application as photo-sensitizers to produce singlet oxygen. The reactions involving singlet oxygen are widely used in various fields of research, such as; organic synthesis, environmental remediation and photo-assisted photodynamic therapy. In this work we prepared doped conjugated polymer NPs containing a series of organic and inorganic dopants by controlled precipitation in both water and acetonitrile, yielding particles of 30 to 50 nm average diameter. Photo-induced generation of singlet oxygen by these particles was studied with a variety of techniques such as: oxidation kinetics of well known singlet oxygen chemical traps followed by substrate and oxygen consumption using UV-Vis spectroscopy and potentiometry, respectively. In addition singlet oxygen was directly detected by monitoring its emission centered at 1270 nm. The results highlight the ability of these NPs to generate singlet oxygen in aqueous medium and its potential use in photo-degradation of organic aqueous pollutants.

Supramolecular nanophotochemistry: excited state behavior of proton transfer compounds in a confined medium

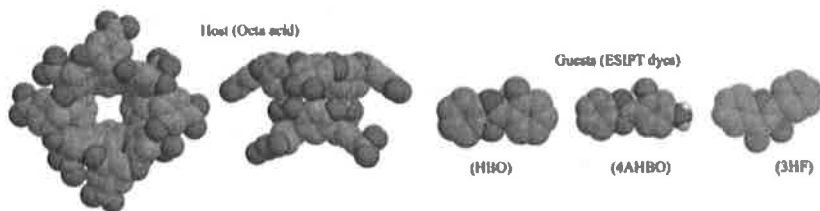
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Proton transfer dyes are being investigated in a confined environment (octaacid) aiming at modifying their excited state properties. In this work we present results of our studies on the excited state behavior of ESIPT compounds that exhibit excited state intramolecular proton transfer (ESIPT) in solution and within the water soluble supramolecular host octaacid (OA) using steady-state and time resolved fluorescence emission spectroscopies. The formation of the 2:1 host:guest complexes was evident from ¹H NMR titration signals. This work demonstrates that the OA capsule provides an opportunity to explore the excited state behavior of sparingly water-soluble proton transfer dyes in water.



Micro-heterogeneous systems containing non-ionic surfactants derived from mono and disaccharides

Germán Günther Sapunar

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Non-ionic surfactants have shown to be a good alternative for the non-biological detergents. A particularly interesting group of surfactants are the fatty acid esters of monosaccharides and disaccharides. These surfactants have unique properties: they are non-toxic, skin compatible, non-polluting and biodegradable, accompanied by outstanding surface-active properties (surface tension-reducing capacity, penetrability into lipid bilayers, easiness of dispersion, and remarkable emulsifying power, among others) Moreover, their synthesis usually involves renewable sources.

The raw materials involved in their synthesis are low cost, simple, effortlessly accessible and renewable (independent from the petrochemical industry). These non-ionic surfactants have a large number of applications in many fields such as cosmetic and health care. Like food additives, they have a very large variety of functions such as emulsifying, foaming, improving components mixing, improving water holding, preventing denaturation, avoiding precipitation. Sucrose esters with short hydrocarbon chain are widely employed to solubilize membrane proteins without causing denaturation, to extract specific compounds (i.e. enzymes, receptors and transport carriers), and they can be removed by simple dialysis. In the field of drug delivery, glycolipids are used to modify liposomes and target them to specific cellular locations.

The presence of the bulky and highly hydroxylated heads, confers an important degree of structuration to the water near the bilayer, an important and relevant parameter related with the interphase of the microstructures formed, especially in the case of the small water pools of reversed micelles or mixed micelles.

By employing photophysical and photochemical procedures, we characterized the physical chemical properties of the different micro-heterogeneous aggregates formed by Sucrose esters (micelles and reversed micelles). Additionally, we studied the changes on the properties of model bilayers and erythrocytes produced by the interaction with several glycolipids. As a model bilayer we used SUVs (small unilamellar vesicles) and GUVs (Giant unilamellar vesicles) and as natural membrane we use erythrocytes with different cholesterol

content. Two-photon microscopy and Laurdan as a fluorescent probe was employed to characterize the membranes.

Financial support from Fondecyt 1120196 and 1140454

Advanced processing of materials with femtosecond laser pulses

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Femtosecond laser micromachining has been used as an interesting approach to process materials, aiming at applications in micromechanical actuators, photonic devices and biology. The nonlinear nature of the light-matter interaction achieved with femtosecond pulses confines the induced changes to the focus of the laser beam, which allows fabricating complex three-dimensional micro/nano structures with special properties. In the last few years, different laser fabrication methods have been used to obtain photonic crystals, waveguides and, more recently, scaffolds for biological applications. Our work has been focused on developing strategies to produce microstructures, by fs-laser-microfabrication, containing active components. To explore possibilities in this direction, we fabricated active microstructures using two-photon polymerization with interesting optical and biological properties. To illustrate the potential of this approach, we present the microfluorescent devices, waveguides containing metal nanoparticles, micro-optical storage devices and microstructures for biological applications. Experimental results on the optical properties, as well as on the bio-related applications were carried out, indicating the approach proposed here as a promising alternative for the fabrication of microstructures for applications in displays, optical storage, waveguides, drug delivery and tissue engineering.

Integrated super-resolution optical and scanning electron microscopy: towards investigating local interactions of single molecules and dna functionalized nanoparticles

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The structure and organization of nanomaterials, such as nanoparticles (NPs), has a large impact on their physical and chemical properties. By altering the nano-scale arrangement and configuration of metal NPs, e.g. through the use of DNA mediated templating and surface attachment, the plasmonic properties of self-assembled structures can be tuned to a great extent. Therefore, the plasmonic properties of metallic nano-assemblies can in principle be engineered for specific applications. However, the intimate link between structures and plasmonic properties is not fully understood. Here, we will apply unique integrated super-resolution optical and scanning electron microscopy to correlate the structure of DNA mediated assembled NPs with their plasmonic properties. More in particular we intend revealing under *in situ* conditions plasmon-related interactions between NPs and molecules by means of plasmon-enhanced fluorescence or surface-enhanced Raman. As such, the integrated microscopy will provide novel structure-function insights into the overall mechanism of plasmon-enhanced phenomena with an unprecedented detail. In addition to that, many structure-related photochemical process on surfaces can also be studied.

Photo oxidation mechanism of coumarin dyes

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Coumarins have been widely used to design fluorescent probes with different purposes including directly detection of free radical formation and evaluation of antioxidant properties of phenols in complex systems [1-2]. In the last few years, we have noticed that under extreme oxidation conditions the kinetic obtained with these probes may become very complex. In fact, 7-amino coumarins behaves highly reactive to free radicals beyond their electrochemical properties determined in aqueous media but surprisingly it is obtained a similar oxidation pattern that in photolysis with visible light irradiation. The photochemical oxidation of these coumarins in organic solvents is in agreement with an oxidation process induced by triplet excited state formation. Laser flash photolysis experiments permitted to detect triplet species (λ_{max} 500-550 nm) and to evaluate their reactivity toward molecular oxygen generating coumarin derived free radical species. In aqueous media, it is generated a free radical cation (λ_{max} 370 nm) in a photo ejection process triggered by two consecutive photon absorption. Coumarin photolysis under stationary conditions also responds to a free radical cation formation by auto oxidation enhanced during light irradiation. Interestingly, in aqueous media the coumarin oxidation induced by these oxidant intermediates is only explained by participation of cinnamic acid form derived from coumarin hydrolysis in equilibrium with close coumarin.

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Acknowledgments

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Design of drug delivery system for active compounds used in treatment of cancer, tissue engineering and neuro-degenerative diseases

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The ability of the body to restore its integrity subsequent to many different kinds of injury is essential for the maintenance of life. Any living organism, in its constant interaction with the environment and with other organisms, eventually faces adverse situations, such as, infections or many other diseases as Cancer, Parkinson Alzheimer and other that might to be treated to repair or reconstitute its body structures in order to preserve the original tissue function. Today there are a new field of medicine that are in charge of the development of these new techniques and therapeutic approaches to repair and restore cells, tissue and body integrity know generally as Tissue Engineering. More specifically the studies in Tissue Engineering in the center recently inaugurated has conditions to reproducing in scale a skin scaffolds, done of biopsy of own patient's cells or from a cell bank in conditions of using this system for the treatment of wound healing diseases, burned skin and other cutaneous pathologies. The innovation in the association of photoprocess with photoactive compounds when incorporate in the models, will allow us to modulate the regeneration of the tissue increasing the wound healing process reducing the rejection allowing the best rebuilding of the damage cutaneous tissue. The same strategy of combining Light and Nanotechnology have been studied during the treatment of Glioblastoma, under clinical procedure, what open a new field in the studies of Neurodegenerative diseases.

Defined as a therapeutic approach that use biomaterials in association with small molecules, cells lines, genes, or other biological material to maintain, replace, or repair organ function with the objective of correcting the underlying pathology already mention. Most of the work developed until now are based on the use of engineered cells, tissues, associated with photoactive materials that can potentially extend and improve a patient's life. Cancer and many other non-oncological diseases has been used nanotechnology associate with the development of DDS and photoprocess to improve the treatment of clinical protocol to treat skin cancer and other cancers. The association of tissue engineering models, nanotechnology

and photoprocess (drugs working by light activation- PDT) will be discuss in this talk, presenting the future advantages of these combination not only applicble to cancer treatment, but also to other diseases, as neuro-degenerative diseases.

Pre-fluorescent probes in micro-heterogeneous media: dusting up traditional knowledge

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It is well known that paramagnetic nitroxides are efficient quenchers of singlet-excited states of fluorophores. The way to make this quenching even more efficient is to link the fluorophore covalently to the nitroxide moiety, converting this interaction to an intramolecular process. This intramolecular quenching can be annihilated when the free radical (nitroxide) reacts with a hydrogen donor to become a diamagnetic structure. From some time we have been interested in preparing pre-fluorescent probes to mainly monitor hydrogen transfer reactions from phenols (antioxidants). Since the disappearance of the radical nitroxide is concomitant with the restoration of the probe fluorescence, the process can be monitored by both fluorescence and/or electron paramagnetic resonance spectroscopy. Thus, the use of pre-fluorescent probes has become a powerful and versatile tool to monitor in situ biological processes mediated by free-radical species. However, since the biological media present heterogeneous environments these methodologies could provide misleading information about the activity of these molecules when these environmental factors are not properly taken into account. For example, we have observed a subtle effect based on different orientations of the radical probe within a micellar interface, which change the quenching rate constant of a fluorophore by a nitroxide-based probe of variable hydrophobicity. Our investigations have allowed us to explain what is called a "cut-off effect", described previously for series of antioxidants of increasing lipophilicities in microheterogeneous environments.



XII ELAFOT
2015, Maresias - SP, Brazil

TECHNO-SCIENTIFIC LECTURES

TEC1 – TEC2

Advanced optical analysis in materials science

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Horiba Scientific

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Optical analysis refers to the broad and general process by which a material's structure and properties are probed and measured. It is a fundamental process in the field of materials science, without which no scientific understanding of engineering materials could be ascertained. The mean of the term can be differ; some definitions limit the term's use to techniques that study the microscopic structure and properties of materials, while others use the term to refer to any materials analysis process including macroscopic techniques such as mechanical testing, thermal analysis and density calculation. The scale of the structures observed in materials characterization ranges from angstroms, such as in the imaging of individual atoms and chemical bonds, up to centimeters, such as in the imaging of coarse grain structures in metals. While many characterization techniques have been practiced for centuries, such as basic optical microscopy, new techniques and methodologies are constantly emerging. In particular the advance of some micro-techniques such as Raman and Fluorescence spectroscopies, Photoluminescence and Electroluminescence has revolutionized the field. These techniques allow the imaging and analysis of structures and compositions on much smaller scales than was previously possible, leading to a huge increase in the level of understanding as to why different materials show different properties and behaviors. More recently, atomic force microscopy has further increased the maximum possible resolution for analysis of certain samples.

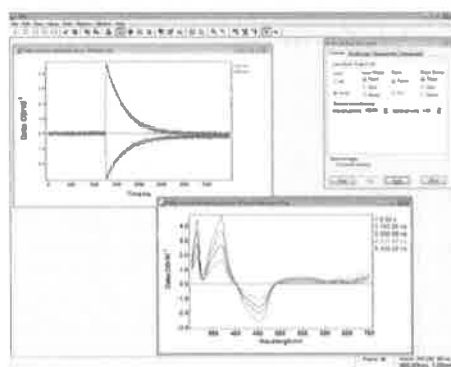
TEC2

Turn-key nanosecond transient absorption spectroscopy; co-utilization of iccd, pmt, and ingaas detectors for flash photolysis and upconversion laser-induced luminescence

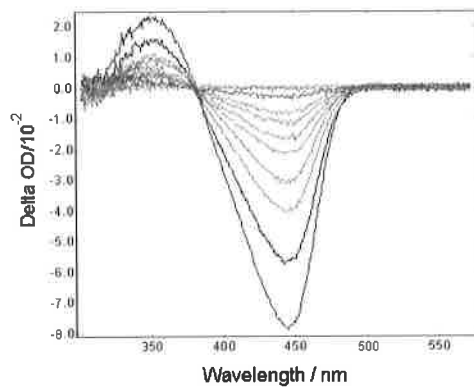
Ian N. Stanton

Application and Technology Specialist, Edinburgh Instruments Ltd

This presentation will feature the basic technique of transient absorption (flash-photolysis), and the measurements made possible by a state-of-the-art, turn-key instrument; the Edinburgh Instruments LP980. The LP980 can record kinetic and spectral transient data using PMT, InGaAs, and ICCD detectors, allowing for unlimited transient measurement capabilities. Other uses for such an instrument, such as laser induced fluorescence (LIF), transient Raman, and laser induced breakdown spectroscopy will be expanded, with special attention given to lanthanide-based upconversion luminescence lifetimes using an ICCD camera.



Kinetic and Spectral Data operations in a single software package



Spectral transients of the photocycle of photoactive Yellow Protein over the timescale of 50
– 500 ms measured on an ICCD camera.



XII ELAFOT
2015, Maresias - SP, Brazil

ORAL COMMUNICATIONS

OC1 – OC10

Electrochemical polymerization of edot substituted phthalocyanines. Its applications as photoelectric and electrochromic materials.

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The employment of organic materials in the development of solar cells, organic light emitting diodes, electrochromic cells, is one of the most active research areas in materials science. Many studies on the development of electronic and energy conversion materials incorporate phthalocyanines, chlorophyll derivatives, and related tetrapyrrolic compounds, due to their participation in the photosynthesis process and their unique electronic, magnetic and optical properties. Thin films exhibiting high conductivity that are fabricated through the electropolymerization of electroactive monomers are potential alternative materials for the preparation of highly efficient devices. The use of electrogenerated films has the advantage of being synthesized in one-step, which allows fine control over the film thickness, an important parameter when fabricating optoelectronic devices.

Thus, the electrochemical polymerization of suitable Phthalocyanines monomers can be an appropriate way for the production of optoelectric films. Phthalocyanines can be easily modified with electropolymerizable groups in order to obtain thin films for applications in different fields. On the other hand EDOT has been used as building blocks in the generation of polymers because they are excellent hole transport materials. In this work we present the formation of new films generated by electropolymerization of EDOT substituted Phthalocyanine monomers. The films were generated and characterized by cyclic voltammetry, UV-vis spectroscopy and, spectroelectrochemistry. An electropolymerization mechanism that involves coupling of two EDOT radical cations is proposed. As a result, Phthalocyanines connected by EDOT dimmers are obtained. The films showed the generation of photocurrents under illumination, and also presented different colors during oxidation/reduction cycles.

Soybean phosphatidylcholine liposomes as a tool to study peroxidation photoinduced by pterin

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Lipid peroxidation (LP) is involved in many physiological and pathological events [1, 2]. The main compounds of biological membranes, phospholipids containing polyunsaturated fatty acids (PUFA), are predominantly susceptible to the process of LP that includes as a first step, a hydrogen atom abstraction. Liposomes can be used to learn more about issues that cannot be studied in biological membranes. On the other hand, pterins, heterocyclic compounds derived from pterin (Ptr), can be found in biological systems in many forms and playing different roles (pigments or enzymatic cofactors for numerous redox and one-carbon transfer reactions). They act as photosensitizers under UVA radiation on biomolecules such as nucleotides, plasmid DNA, amino acids, proteins [3, 4]. In addition, it has been found that pterins have phototoxic effect on cell culture [5]. Sonicated liposomes of soybean phosphatidylcholine (SoyPC) were prepared in buffer Tris containing pterin. The location of pterin in the liposomes was investigated by size exclusion chromatography and absorption/fluorescence spectra. Later on, liposomes were submitted to LP, under air atmosphere and UVA irradiation, with Ptr as a photosensitizer. Conjugated dienes and trienes were determined by absorption at 234 and 270 nm, respectively. Mass spectrometry was used to identify peroxidation products. As a conclusion, steady UVA irradiation of solutions containing Ptr and SoyPC led to peroxidation of PUFA, whereas the Ptr concentration remained unchanged. Ptr showed an enhanced effect on peroxidation rate and steady state concentration of oxidation products. This model constitutes a valuable system to study LP intermediaries and products in an aqueous environment and to determine the effect of Ptr as photoinducers.

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Evaluation of the effects of both photosensitizers and quenchers of singlet oxygen on hela cells using synchrotron infrared microscopy

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In order to better understand the PDT mechanism, synchrotron infrared microscopy was used to detect the associated intracellular biochemical modifications following the irradiation of HeLa cells incubated with β -carotene or imidazole as typical hydrophobic and hydrophilic quenchers, respectively. For this purpose, Photodynamic Therapy (PDT) at many concentrations of the quenchers was performed. The use of the synchrotron source allows the analysis of biological components in the cell at subcellular resolution. The IR spectra of PDT-treated, PDT plus quencher-treated and control HeLa cells were recorded at the SOLEIL Synchrotron Infrared beamline targeting specifically the cell nucleus. Principal component analysis (PCA) has been used to assess the IR spectral changes between the various HeLa cells spectral data sets (The Unscrambler software, CAMO). PCA revealed that there is a frequency shift of protein amide I and amide II vibrational bands, indicating changes in the protein secondary structures of the PDT-treated cancer cells compared to the control cells. In addition, the scores in those cells treated with any quencher appear to be similar to the controls indicating a photoprotective effect.

OC4

Circadian control and the ecological niche surrounding bioluminescent mushrooms

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Over the past decade, the mechanistic nature of fungal bioluminescence has progressed and the enzymatic basis confirmed. While the important question of 'how' fungi bioluminesce is being answered, the question of 'why' they glow has remained unanswered for eons. Recently, work performed by our lab and collaborators has demonstrated that fungal bioluminescence is under circadian control, with light emission greatest around midnight. Likewise, the quantities of active fungal luciferin reductase, fungal luciferase, and fungal luciferin are similarly regulated. This circadian regulation implies function. Evidence is accumulating from ecological studies that suggest different arthropods are attracted to bioluminescent mushrooms during the night. Attracted arthropods are likely involved with diaspore dispersal and defense.

Aggregation induced absorption (aia) and/or emission (aie) based on gold supramolecular systems

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Supramolecular gels, and particularly supramolecular hydrogels, have recently become a hot topic in materials chemistry. This is mainly due to their great potential for the creation of stimuli responsive systems for diverse applications, ranging from optoelectronics and light harvesting to regenerative medicine and drug delivery.[1] Apart from the well-known weak interactions of the organic molecules, metal•••metal interactions have been found to further stabilize the metallogels and give rise to interesting spectroscopic properties. In this respect, we recently reported on the formation of luminescent Au(I) hydrogels with organometallic alkynyl complexes where aurophilic (Au•••Au) intermolecular interactions must be involved on the gelation process.[2-4] In general, weak intermolecular interactions should play an important role on molecular recognition processes.[5] In this kind of supramolecular structures, the aggregation process can be favoured or destroyed in the presence of external analytes and this process can be followed by absorption (AIA) and/or emission (AIE) techniques (Scheme 1). In the particular case of gold(I) systems, we have explored how aurophilic interactions and the consequent spectroscopic properties are affected by changes on aggregation process in the presence of anions or cations. Scheme 1. Graphical representation of AIA or AIE based on Au(I) supramolecular systems.

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Asphaltene structure by fluorescence quenching

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Asphaltenes are the heaviest, less soluble and more polyaromatic fraction in petroleum. Also, this the most polar fraction of crude oil, containing heteroatoms like N, O and S, metal ions and a C / H ratio close to 1. The asphaltenes are a solid soluble in the oil but insoluble in alkanes like pentane and heptane. This petroleum fraction imparts high viscosity to the oil and is deleterious to all steps in petroleum production and transformation. The chemical nature of this fraction is still under debate and the structure elucidation is very important for the entire society. Photochemical technics can be applied in order to elucidate missing information. For all these features this study aims to use the fluorescence of asphaltenes from a Brazilian crude in order to improve the present model. Here was applied time resolved fluorescence to evaluate the structural characteristics of asphaltenes, using organometallic complexes, based on 8-hidroxyquinoline, as quenching probes. Our results indicate that the asphaltene fluorescence quenching can not be explained by a planar structure model.

Power dependence of visible upconversion luminescence in binary Gd_2O_3 : CeO_2 hosts doped with Er(III) / Yb(III) under infrared excitation.

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INQUIMAE /FCEyN – UBA Buenos Aires Argentina

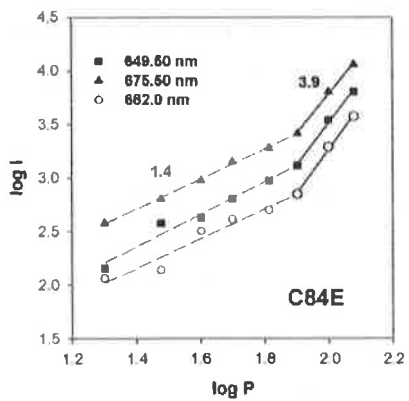
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CeNTech - Institute Of Physics Münster Germany

In this work we show the results obtained from the upconversion (UC) emission spectra of monodispersed monophasic polycrystalline spheres of ca. 200 nm of CeO_2 , Gd_2O_3 and Gd_2O_3 : CeO_2 solid solutions doped with Er(III) and with Er(III) / Yb(III) . Bare Gd(III) rich samples hosts exhibit a c-type (I3a) structure related to Gd_2O_3 lattice; bare Ce(IV) and Ce(IV) rich samples hosts exhibit a $\text{Fm}3\text{m}$ -type related to the CeO_2 one. The dopant levels are 6% in Er(III) with no sensitizer and 5% in Er(III) with 1% Yb(III) as sensitizer. The samples were illuminated with a continuous-wave radiation at a wavelength of 976 nm from a fiber-coupled laser diode. Visible green and red upconversion emission was observed in all the samples under excitation at 976 nm. In the green range, all the samples showed a linear dependence of the logarithm of the emission intensities ($\log I$) with the logarithm of the incident excitation power P ($\log P$), as expected according to the equation: $I \sim P^n$ [1]. On the contrary, the same measurements performed in the red range showed an anomalous behavior for the samples rich in CeO_2 . A change in the slopes was observed at certain power values, as shown in the Figure (C84E means 84% CeO_2 :10% Gd_2O_3 : 6% Er(III)). This behavior was explained in terms of a looping mechanism involving cross relaxation processes among the Er(III) ions [2]. Given that the samples have the same level of dopants, these differences can only be ascribed to the host matrix.

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Accessing the spatial distribution of photostability of materials by photobleaching lifetime imaging microscopy (plim)

Diego Lencione*, Renan Leitão, Loren Trujillo, Rodrigo Albuquerque, Marcelo Gehlen

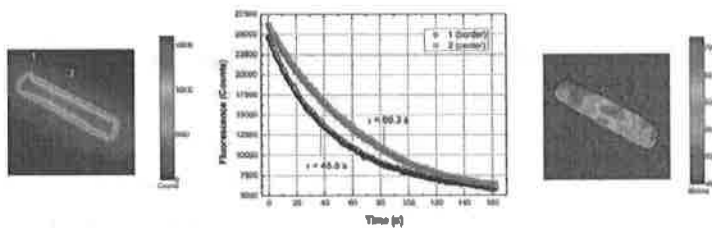
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Photobleaching is a photochemical reaction of a dye or a fluorophore with surrounding molecules that turns it permanently unable to perform cycles of fluorescence. This phenomenon was mainly investigated for substances in the liquid state using a macroscopic approach to determine the average rate (or inversely the lifetime) of photobleaching for solutions. In contrast, few groups have investigated this phenomenon locally with the help of fluorescence microscopy, highlighting the pioneer work of Benson et al. [1] and the recent contributions of Wüstner et al.[2]. By using wide field fluorescence microscopy it is possible to exhibit a spatial distribution of the rate of photobleaching for materials that don't change its spatial position significantly in time. In this work we present a user-friendly computational tool to assist microscope based photobleaching experiments called PLIM, from Photobleaching Lifetime Imaging Microscopy, developed in Matlab®. With this tool is possible to generate: the average image from a sequence of fluorescence images; the photobleaching lifetime image calculated by mono or bi exponential fitting; the average value of photobleaching lifetime; the standard deviation; the fitting residuals as well as exporting facilities. We have used this tool to investigate the photobleaching processes in zeolite L systems homogenously hosted with thionine dye, in function of excitation irradiance and controlling the sample atmosphere with air, Argon and N₂, to determine locally the effects of O₂ availability and excitation irradiance for the photostability.

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Z-e isomerization of azobenzenes catalyzed by bare and core-shell gold nanoparticles

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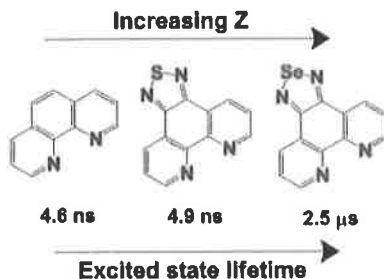
The interaction of metallic nanoparticles (MNPs) with azobenzenes (ABs) has received considerable attention in view of the changes that the photochromic transformation confers to NP properties and photocontrollable layers on metal surfaces. MNPs can deactivate the electronic state of organic molecules placed near their surface, modulating the switching capability of the probe. Not so well studied is the isomerization kinetic rates of azobenzenes placed near MNPs. Scaiano et al. were the first ones to report the AuNP catalysis of the thermal Z-E isomerization of unbounded ABs in suspensions of 'pseudo-naked' AuNPs. They reported average rates in AuNP suspension in water. Here we examine the kinetics of the thermal Z-E isomerization of ABs in AuNPs suspensions to answer the questions: Which is the magnitude of the catalytic effect of the AuNPs? Can we obtain the Z-E thermal isomerization rate of azobenzenes over the AuNPs? Which is the role of the metallic surface? Is it necessary for the photochromic compound to be in direct contact with the metallic surface or does the NP influence on the catalysis extend in volume due to the high polarizability of the NP plasmonic interaction? We explored the catalytic effect of 15 nm diameter AuNPs upon the thermal Z-E isomerization reaction of azobenzene and nine 4 and 4-4' substituted azobenzenes (ABs). The kinetics follows a first order rate in a range of $[ABs] = 5$ to $50 \mu M$ and $[AuNPs] = 50 pM$ to $1 nM$. A kinetic analysis of this compartmentalized system renders the thermal Z-E isomerization rate constant associated to each AuNP, which is 10 to 10^6 fold higher in comparison to the same free ABs in solution. Experiments with selective Au facets coverage, as well as the kinetics studied in gold-silica core-shell nanoparticles ($AuNP@SiO_2$) of different thickness, demonstrate the surface nature of the catalysis and allow to evaluate the diffusion coefficient of AB in the silica layer.

The effect of spin-orbit coupling on selenadiazolo- and thiadiazolo- fused 1,10-phenanthrolines

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Phenanthroline derivatives have been widely studied for many practical applications. When fused with either a selenadiazole or a thiadiazole unit and used as ligands to produce metal complexes, those present unique photochemical and magnetic properties. In this work, a detailed theoretical description (using TDDFT and CASSCF) of the electronic structure of these ligands is presented to explain their unique photochemical and photophysical properties. In particular, the heavy atom effect on the spin-orbit coupling is evaluated, and it is shown to have a major influence on transitions between the excited states of [1,2,5]selenadiazolo[3,4-f][1,10]phenanthroline. The appearance of a long lived emission under inert argon atmosphere at room temperature is investigated through both theoretical and experimental methods. Photocurrent experiments demonstrated that these specific properties of the [1,2,5]selenadiazolo[3,4-f][1,10]phenanthroline are promising for photovoltaic applications (Dyes and Pigm.; GALLARDO et al., 2015). Due to their long excited state lifetime and electronic properties, DNA photocleavage studies using these ligands and some of its complexes of Fe(II) and Ru(II) were conducted and revealed an unusually high activity under visible and UV light, with almost complete DNA conversion to Form III in about 5 minutes of irradiation (Chem. Comm., de Souza et al., 2010). The mechanism through which these processes occur and other experimental results are discussed. It appears that a direct oxidation of the DNA is the main cause of cleavage and that it is oxygen independent with a very low activity in dark.



XII ELAFOT
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POSTERS

Fluorescence anisotropy decay of perylene diimide complexes aggregates: optical properties in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution

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In natural photosynthesis, the chlorophyll acquires structure in a staggered fashion for coordinating the metal ion and proteins, providing a packaging-type J. This packaging facilitates the absorption and transport of electrons in the molecular network. Thus, materials that exhibit J aggregation type are promising candidates for application in artificial photosynthesis. In this context, we are interested in following how the coordination of perylene derivatives to Ru(II) (complex I) and Ru(II)-Mn(I) polypyridine complexes (complex II) can form aggregates and what type of structure is preferentially produced. This work describes the experimental conditions for the formation of aggregates of transition metal complexes. The experimental techniques employed are UV-vis absorption, fluorescence steady state and time-resolved (ps order), and fluorescence anisotropy of fluorescence correlation spectroscopy (FCS). Complexes I and II have appreciable solubility in most organic solvents tested. For the free perylene changes in the absorption peaks and the molar absorptivity values with the variation of the solvent are not expected. Apparently none of complexes exhibited aggregation effect on the following medium (acetonitrile, acetone, dichloromethane, ethanol, methanol, dimethylformamide, dimethylsulfoxide). Moreover the ratio of the intensity of the perylene transitions $0 \rightarrow 0$ and $0 \rightarrow 1$ of 1.34 to 1.26 in complex I in II may be derived from the presence of metal or a fragment interaction π - π "stack" in II. The steady state spectroscopic (UV-vis and emission) studies showed a dependence on the concentration changes of complexes. The emission spectrum exhibited an enlargement of the bands and a decrease in the ratio of intensity of transitions of the perylene moiety $0 \rightarrow 0$ and $0 \rightarrow 1$ suggesting formation of aggregates. Formation of aggregates was also observed through fluorescence decay as a function of concentration: the higher the concentration the higher the τ_0/τ_1 ratio. Moreover, aggregation was also confirmed by experiments conducted in solvent mixtures $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and in anisotropy experiments. The self-aggregation decreases the coefficient of light absorption and in particular affects the definition of the vibrational

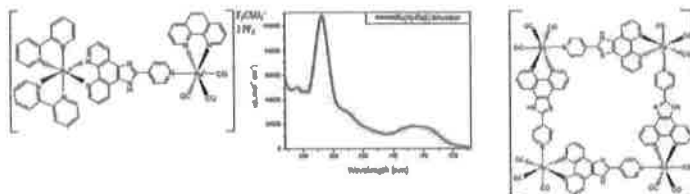
levels of the bands 0-0, 0-1 and 0-2 of the derivatives of perylene and can lead to appearance of new bands in the absorption spectra and/or emission spectrum.

New multi-metallic architectures: developing new luminescent ligands

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The electronic absorption of a molecule can lead to the emission of light by fluorescence and/or phosphorescence. In the case of phosphorescence, when the molecule is excited, a change occurs in the multiplicity of spin: spin inversion takes place and the molecule goes from one singlet excited state to a triplet excited state. The energy from this excited state may be transferred to another molecule which exists in the triplet state, whether or not excited. This project aimed to investigate the synthesis and spectroscopic characterization of new dppz-type ligands. Synthesis and spectroscopic characterization of Re (I) and Ru (II) complexes with dppz-type ligands as ligands. Subsequently, assessed the reactivity of Re (I) and Ru (II) when these metals form dimers and assembling Re(I) complex with four metal centres of Re. Finally we evaluated the photophysical properties of the ligands and complexes. The signals of the binuclear Ru(II)-Re(I) in the $^1\text{H-NMR}$ were seen in the region between 8.0-10.0 ppm assigned to H that are present in aromatic systems . This complex features intense absorption at 280 nm and 443nm, attributed to IL and MLCT transitions, respectively. Furthermore, the dimer showed an emission at 390 nm and 615 nm and lifetime equal to 164 ns (with excitation wavelength of 495 nm). Regarding to the four metal centres of Re(I), the $^1\text{H-NMR}$ for this complex showed an up shift equal to 0.5 ppm for the aromatic H when compared to its mononuclear precursor. This complex had absorption bands at 245 nm, 280 nm, 340 nm and 380 nm. The molecule, when excited at 380 nm, has a broad and intense emission at 545 nm. Kinetic decays measured at ns time showed an emission lifetime of 3.02 ns when using a laser with a 495 nm lamp. The dppz-type ligands were successfully made and the results obtained so far suggest the formation of a molecular square and binuclear species.



The use of luminescent ru(ii) complexes for the diagnosis of alzheimer's disease.

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Alzheimer's disease is a progressive and slow neurodegenerative disorder that primarily attacks memory and cognitive function in the elderly people. This neuronal dysfunction is characterized by the accumulation of β -amyloid peptide in the brain that leads to their aggregation into oligomers and, subsequently, insoluble fibrils, resulting in the formation of senis plates. This work seeks to develop luminescent ruthenium (II) complexes with bioactive molecules in the inner coordination sphere. We hope that the complex interacts with the β -amyloid peptide enabling to monitor the processes of formation and aggregation of this peptide. In the way that the response of this interaction can be accompanied by the change in the complex luminescence in the biological environment. The complex $\text{Ru}(\text{phen})_2(\text{Apy})_2$ was synthesized by the reaction of the $\text{cis-}[\text{Ru}(\text{phen})_2\text{Cl}_2]$ precursor with 2 equivalents of aminopyridine in mixture $\text{H}_2\text{O}/\text{EtOH}$ (1: 1). The composition and structure of the complex was confirmed by ^1H NMR spectroscopy, shown in Figure 1. The UV-vis spectrum of the compound was obtained in the phosphate buffer pH 7.4 is shown in Figure 2 (A), and it shows an intense band at higher energy values mainly associated with $\pi\text{-}\pi^*$ electronic transitions (< 350 nm) and a broadband between 400-550 nm, characteristic of MLCT processes. The excitation was recorded according to the band in the visible region in phosphate buffer pH 7.4 and room temperature, producing a significantly emission with maximum at 655 nm, shown in Figure 2 (B). These experiments conducted so far have shown that the $\text{Ru}(\text{phen})_2(\text{Apy})_2$ complex was successfully obtained and the spectroscopic properties are suitable to study the interaction between β amyloid peptide and the complex.

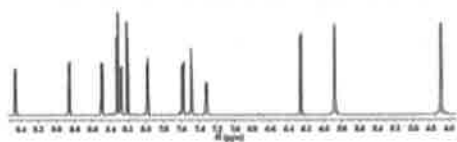
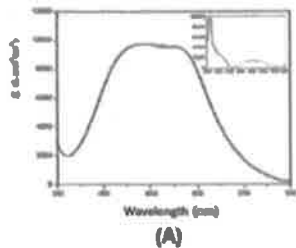


Figure 1. $^1\text{H-NMR}$ spectrum for the complex $\text{Ru}(\text{phen})_2(\text{Apy})_2$



(A)

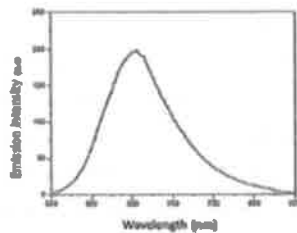


Figure 2. (A) UV-vis spectrum (B) emission spectrum of $\text{Ru}(\text{phen})_2(\text{Apy})_2$ in phosphate buffer pH-7.4

Influence of ions and pH on the hydrolysis of betanin

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Betalains are natural pigments found as yellow betaxanthins or violet-red betacyanins, both originated from spontaneous non-stereoselective addition of amines or amino acids to betalamic acid. Betaxanthins are responsible for visible fluorescence of flowers, e.g., yellow varieties of *Mirabilis jalapa* (four o'clock), whereas betacyanins are natural phenolic antioxidants. Sources of betalains used for food-coloring purposes contain, among other substances, a mixture of betanin (Bn, 2S/15S) and its epimer isobetanin (iBn, 2S/15R). Betanin (CI Natural Red 33, E-code E162, betanidin 5-O- β -glucoside) is almost entirely obtained from red beet crops and is the only betalain approved for use in food. Betanin (Bn) was obtained from red beet juice. The decomposition of Bn in water, phosphate buffer (pH = 2,1, 6,2 or 8,2), acetate buffer (pH = 4,8 or 5,8) and citrate buffer (pH = 4,8) was studied at 85 °C. Buffers were prepared in five different concentrations: 10, 50, 100, 250 e 500 mmol L⁻¹. The half-life of Bn in water is 13.5 min ($k_{obs} = 0.051 \text{ min}^{-1}$). The observed rate constant for the decomposition of Bn depends on both pH and buffer concentration. In phosphate buffer pH = 2.1 the increase in the concentration of the buffer results in a decrease in k_{obs} , whereas in pH > 4, k_{obs} increases with the increase in the buffer concentration. The occurrence of general acid-base catalysis is proposed to rationalize the results. This work was supported by FAPESP, CNPq and CAPES.

Semisynthesis and theoretical study of betalains

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Betalains are nontoxic vacuolar pigments that replace anthocyanins in some families of angiosperms and some basidiomycete fungi. There are two classes of betalains: yellow betaxanthins and red betacyanins both biosynthesized from betalamic acid, a fluorescent aldehyde derivative of L-tyrosine. Betalains are found, for example, in beetroot, dragon fruit, fly agaric, bougainvillea and amaranth. In addition, the petals of yellow varieties of four-o'clock and eleven-o'clock are pigmented by fluorescent betaxanthins. The geometry of the lowest energy conformers (BOMD-PM6, 10 ps) of betalamic acid, betanin (betanidin-5-O-glucoside, Beetroot red, E-162), and indicaxanthin (betaxanthin of L-proline) were fully optimized in gas phase at the DFT M06-2X/6-31+G(d,p) level. Electronic transition energies and oscillator strengths of the molecules were calculated employing the semiempirical ZINDO/S/PCM method or the TD-DFT/SMD method. Theoretical electronic transitions were compared with the experimental data. Betanin was purified from beetroot (*Beta vulgaris*) extract by semi-preparative RP-HPLC. Betalamic acid was obtained by alkaline hydrolysis of betanin and purified by reversed-phase flash column chromatography. Indicaxanthin was semi-synthesized by reaction of L-proline and betalamic acid in aqueous acid media and purified by RP-HPLC. The results of the computational investigation are in good agreement with experimental data. All three compounds studied belong to the C₁ point group and the observed high intensity bands in the visible region arise from HOMO→LUMO transitions and are assigned as $\pi \rightarrow \pi^*$ transitions. Also, electronic properties of betalains are sensitive to conformational changes in the 1,2,3,4-tetrahydropyridine ring. This modeling approach would be useful in the study of betalamic pigments as well as in the design of new derivatives. This work was supported by FAPESP, CNPq, CAPES and Natura Cosmetics.

Investigation of structural changes of sds/n-butanol mixed micelles by viscosity, refractive index and fcs techniques

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Surfactants are commonly used in the presence of additives to improve their properties. Among them, n-alcohols have been widely used as cosurfactants. In this contribution, we propose the study of the butanol effect on the growth of SDS micelles. For this purpose, we combined bulk techniques as viscosity and refractive index with fluorescence correlation spectroscopy (FCS), a technique at single-molecule level, to predict changings in the micellar structure caused by the addition of low concentrations of alcohol. The micellar volumes were calculated from viscosity measurements using adaptations of the Einstein's equation and from refractive index measurements using a modified Clausius-Mossotti's equation. The volumetric ratio of about 100 indicated that the viscosimetric volume is related to the hydrodynamic volume, including the micellar hydration layer, and the refractometric volume is related to the hydrophobic core. From these volumes, one can obtain the diffusion coefficients of the mixed micelles using the Stokes-Einstein's equation. The diffusion coefficients using bulk techniques were found in the range of 9.3 to $4.5 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$. These results shows evidences of a contraction of the Gouy-Chapman layer, because of the strong interaction of butanol molecules situated in the hydrophobic core with the water molecules from the hydration layer. By FCS, the diffusion coefficients continuously decreased upon the addition of butanol. Additionally, the values were about two-fold lower. These values may be related to the micellar volume without the hydration layer, because of the electrostatic interaction between the negative micellar surface and the positive charged rhodamine dye, which displaces the water molecules. Therefore, FCS has presented great potential to study in details micellar dynamics in the presence of alcohol.

Fitoquímica e fotoquímica: uma relação didática

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Há tempos que diversas pesquisas são feitas à procura de métodos eficazes de produção sustentável e de baixo impacto ambiental de energia elétrica. Dentre os métodos alternativos destacam-se as células solares, sendo que um dos maiores desafios nesta área é a busca por moléculas com alta capacidade de captar energia eletromagnética na região de maior incidência do espectro solar sem que haja fotodegradação da molécula captadora. A biodiversidade vegetal, ainda, em grande parte, carente de registro e descrição científica, é objeto de estudo dos botânicos e, do ponto de vista de seus constituintes químicos, dos fitoquímicos. Estes estudos indicam que alguns tipos de porfirinas e seus derivados poderiam ser bons candidatos para utilização em células solares, conhecidas com células de Grätzel. A planta *Talinum triangulare*, ou carirú, usada no Norte do Brasil como alimento, tem sido estudada no Dep de Química-UFRRJ e tem alto índice de produção de metabólitos secundários baseados em porfirinas. O presente trabalho resultou de uma parceria com o Jardim Botânico-UFRRJ, interessado em divulgar à população e visitantes as aplicações práticas e alternativas dos produtos de origem vegetal. Foi desenvolvido um protótipo de célula solar com extrato de feofitinas que gerou uma voltagem aproximada de 0,5 V quando exposta ao Sol. A extração de folhas de *T. triangulare* com acetato de etila forneceu uma fração contendo, principalmente feofitinas. Para construção da célula foram usadas duas lamelas de vidro condutor (ITO, óxido de índio dopado com estanho), pasta de TiO_2 em etileno-glicol e extrato de feofitinas foram aplicados a uma das lamelas e grafite à outra. As duas lamelas foram montadas em sanduíche, e solução aquosa KI/I_2 foi pingada, em contato com o TiO_2 . Exposta ao Sol, a célula gerou uma voltagem de 0,47 V, medidos com multímetro. Esta experiência multidisciplinar simples permitiu demonstrar, na semana de IC da UFRRJ, tanto a estudantes de Biologia (botânica), quanto de Química (fotoquímica), a interligação entre estas áreas. A apresentação desta demonstração em escolas de ensino médio está sendo preparada.

Spectroscopic investigation on the interaction between 1,2- and 1,4-naphthoquinones and human serum albumin

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Francisco A Silva ¹, Dari Cesarin-Sobrinho ¹

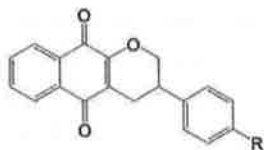
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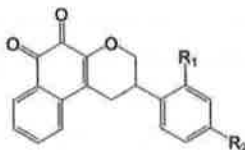
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Serum albumins found in the blood plasma are abundant transport proteins of endogenous and exogenous compounds. It is known that drug-protein interaction greatly influences the absorption, distribution, metabolism and excretion of drugs in the organism. In this work, the interaction of a number of pyran derivatives of 1,4-naphthoquinones (14LPH; 14LPH4Me; 14LPH4Cl; 14LPH4F) and 1,2-naphthoquinones (12LP; 12LP4Me; 12LP24Me; 12LP4Br; 12LP4Cl) with human serum albumin (HSA) was studied employing fluorescence quenching, UV-vis absorption spectroscopy and circular dichroism (CD). The experimental results were analyzed according to Stern-Volmer, modified Stern-Volmer and van't Hoff equations, from which it was possible to obtain the fluorescence quenching rate constant of HSA by the naphthoquinones (k_q), the association constant for the naphthoquinone/HAS system (K_b) and the number of binding sites in HSA (n). Furthermore, the thermodynamic parameters, ΔG° , ΔS° and ΔH° obtained from the fluorescence quenching studies indicated that hydrophobic interaction and hydrogen bonding played a major role in the naphthoquinone/HSA association. Finally, circular dichroism spectroscopy clearly indicated a decrease in the alpha-helix % on the secondary structure of the protein upon its interaction with all 1,4- and 1,2-naphthoquinones.



14LPH R=H
14LP4Me R=CH₃
14LP4Cl R=Cl
14LP4F R=F



12LPH R₁=R₂=H
12LP4Me R₁=H, R₂=CH₃
12LP24Me R₁=R₂=CH₃
12LP4F R₁=F, R₂=H

Time-resolved investigation of all-trans-retinoic acid ultrafast excited state dynamics by femtosecond transient absorption

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Organic compounds with biological properties such as retinoids, carotenoids and flavanoids have emerged as potential candidates for applications in bio-photonics devices due to its capacity to convert optical signals into biochemical events serving as ultrafast electro-optical device. For instance, retinyl molecules are key chromophores found in the opsin as a retinal Schiff base acting primarily as a photon receptor and, subsequently, as light transducer in nervous impulses via cis→trans photoisomerization. Among the retinyl polyenes, the all-trans retinoic acid (ATRA) has not attracted great attention of the investigators from the photophysical point of view. The molecular structure of ATRA has five c=c double bonds in its polyenic backbone connected by a carboxylic acid and a β-ionone group in their extremities, a structural analogue of carotenoids with a fewer number of conjugated c=c double bonds. To shed more light about the electronic structure, in special to the ¹A_g-like state, of the ATRA in solution, we have measured the excited-state absorption (ESA) for ATRA in DMSO solution by using the white-light femtosecond pump-probe technique. Within the temporal resolution of our experimental set-up (~ 200 fs), we observed a mono-exponential decay of S₁ with a 3 ps characteristic time. This decay constant was obtained from the transient signal at the peak of the ESA band located at 535 nm.

Development and characterization of liposome containing zinc phthalocyanine and cisplatin to application as a drug delivery system in pdt.

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Zinc Phthalocyanine (ZnPc) is a promising photosensitizing agent for Photodynamic Therapy (PDT) and its photochemical properties leads to cytotoxicity in cancer cells and high performance photodynamic. ZnPc is the highest lipophilic drug of this second generation that helps its location in the plasma membrane, in microsomes and in mitochondria. However it still need a drug delivery system (DDS) to improve it target-specific to the tumor. Cisplatin is widely used at oncology clinical in cancer therapy, but promotes severe disadvantages such as lack off appropriate tumor selectivity and induce of multi-drug resistance. Liposomes have been used as an efficient DDS in order to increase the selectivity and biodistribution by many drugs. The aim in study was to develop and characterize a novel liposome containing ZnPc for future application in PDT associated with Cisplatin in the same system. The preparation method was the ethanolic injection at 57°C. The lipids used was 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1-2-distearoyl-sn-glycero-3-phosphocholine (DSPC) and cholesterol (Chol). The liposomes were prepared with DOPC/DSPC/chol at the proportion of 0.34: 0.34: 0.31 (mol %) in phosphate buffer saline (PBS), pH 7.4, in the absence and presence of ZnPc at 5 µM. The characterization of liposomes was performed by dynamic light scattering (DLS), electrophoretic light scattering (ELS) and uv-vis spectroscopy.

The diameter of liposomes were 120 nm with low polydispersity index (~0.2) at absence and presence of all active drugs and negative surface charge (- 34 mV). Short-term stability studies indicate that the liposome was physically and chemically stable for at least 30 days at 25°C. Spectroscopic studies showed conservation of absorption profile of ZnPc incorporated. These results indicate that liposomes are promising for synergetic PDT, in association with Cisplatin.

Fret based gold nanobeacon for sequence discrimination

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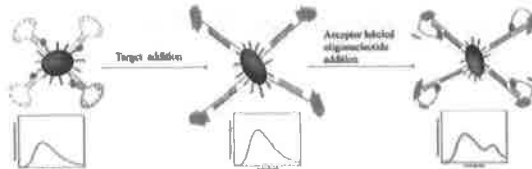
Almada Portugal

We report development of a gold nanoparticle (AuNP) molecular beacon based biosensor coupled to a wavelength shift mediated by FRET, for the detection of fusion transcripts associated with the development of Chronic Myeloid Leukemia. Citrate capped 14 nm gold nanoparticles were functionalized with thiolated polyethylene glycol and further functionalized with a donor fluorophore labeled ssDNA with a hairpin structure. In the absence of a complementary target, the donor is in close proximity to the surface of the gold nanoparticle, leading to its quenching - gold nanoparticles are known to be fluorescence modulators [1-2]. Upon hybridization to the target sequence the donor breaks away from the surface of the gold nanoparticles due to the disruption of the hairpin structure, leading to a partial restoration of the donor fluorescence. The disruption of the hairpin leads to the exposure of the palindromic sequence, allowing the hybridization of an acceptor labeled oligonucleotide – See figure 1. With the donor and acceptor in such proximity, FRET occurs leading to a wavelength shift of the hybridization fluorescence signal to wavelengths that are not affected by the high absorption of the AuNP.

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Effect of hydrogen abstraction of nanoparticles of silica with anthraquinone and evaluation for use in cancer therapy

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Silica nanoparticles functionalized with anthraquinone, rose bengal or pyrene by use of an APTS linker were evaluated as lung cancer drugs (SiNPAAP-OCAq, SiNP-AAP-RB and SiNP-AAP-Py, respectively). Our results indicate that SiNP-AAP-OCAq was the most efficient system for promoting apoptosis under the experimental conditions used despite SiNP-AAP-OCAq having the lowest singlet oxygen quantum yield of the evaluated dyes ($\Phi = 0.15$, $\Phi = 0.79$ and $\Phi = 0.86$, respectively). A possible explanation of the results is based on the photoreactivity of the anthraquinone molecule, which shows, in solution, a rapid hydrogen abstraction from appropriate donors [1]. Although the photochemistry of anthraquinone in solution is well documented, there is no literature data, that we are aware of, that investigates the dye photochemistry using the functionalized silica nanoparticles. Initially we considered that diffusion could have a limiting effect upon the reaction rate for hydrogen abstraction and if this were the case this would potentially exclude this mechanism as a possible route for cellular death. Therefore the photochemical reactivity of SiNP-AAP-OCAq towards indol (used as a model for biological substrates) was investigated employing the nanosecond laser flash photolysis technique. Excitation at 355 nm of a degassed suspension of SiNP-AAP-OCAq, in acetonitrile, resulted in the formation of the anthraquinone triplet that was found to be efficiently quenched by indol ($k_q \sim 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$). The results demonstrate that SiNP-AAP-OCAq is able to photosensitize biological substrates by both type I and type II mechanisms.

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Theoretical and experimental studies of excited state intramolecular proton transfer of nsalicylidene-4-chloroaminopyridine

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Due to their synthetic accessibility and readiness to coordinate main group and transition metal ions, salicylidenes represent one of the most extensively used class of ligands in coordination chemistry, having a wide range of applications as molecular switches in optical recording technology, molecular electronics, and computing. These compounds exhibit tautomeric rearrangements due to intramolecular proton transfer between the enolimine (OH) and the ketoenamine (NH) forms in the excited state – ESIPT. The absorption spectrum of N-salicylidene-4-chloroaminopyridine shows three absorption bands in the ultraviolet region (352, 326 and 276 nm), composed mainly of pi-pi* transitions between $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ states respectively. Respective to its emission spectrum profile in DMSO, it was observed two emission bands, each one assigned as (435 (E*) and 535 (K*) nm). For this system besides of the keto-enol balance due to the ESIPT, there is a possible rotation along N-C bond in the ligand framework leading to cis and trans isomers. According to our calculations, in the excited state the most stable conformer is the trans-keto* species. Acknowledgements: FAPESP (grant 2013/16245-2), INEO (MCT/CNPq/FAPESP), CNPq, CAPES and UNICAMP/FAEPEX for financial support and fellowships.

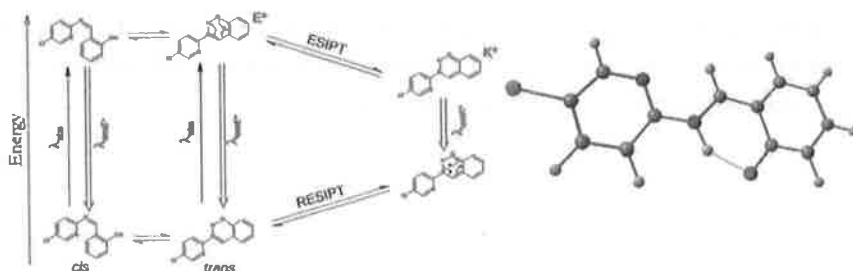


Figure 1. Luminescence mechanism and ligand S_1 trans-keto* molecular structure.

Pluronic f 127 micelles as a platform for controlling the photochemical nitric oxide release from s-nitrosoglutathione

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S-nitrosoglutathione (GSNO) is the most studied primary S-nitrosothiol and is considered to be involved in the storage and transport of nitric oxide (NO) in the body. Although the thermal spontaneous NO release from aqueous GSNO solutions allows its use as a NO donor, promoting the photochemical NO release from GSNO offers a strategy for increasing and controlling the rate of NO release from GSNO, widening its potential medical and pharmaceutical applications. In this study we used Pluronic F127 (PEO-PPO-PEO), an amphiphilic triblock-copolymer which undergoes thermally reversible micellization and gelation. Figure 1 shows the profiles of NO photochemically released from GSNO (100 μ M) in F127 solutions in the concentration range of 10-30 wt% at 15 $^{\circ}$ C and 37 $^{\circ}$ C, measured by chemiluminescence. The solutions were irradiated during 1 h with visible light from a LED source (780 lumens). It can be seen that, after baseline stabilization in the dark, the NO signal increases when the light is turned on, until reaching a maximum and then starts to decrease. At both 15 $^{\circ}$ C and 37 $^{\circ}$ C the rates and the peak values decrease with the increase in F127 concentration and are lower than the values observed in pure water. This stabilization effect can be associated with the presence of F127 micelles in the solutions (20 and 30 wt% F127 at 15 $^{\circ}$ C and all F127 solutions at 30 $^{\circ}$ C). At 37 $^{\circ}$ C the F127 solutions 20 and 30 wt% are in the gel phase and release higher amounts of NO, compared to the same concentrations at 15 $^{\circ}$ C. This result shows that gelation reduces the stabilization effect promoted by the unpacked micelles on GSNO. The stabilization effect of the F127 micelles can be assigned to the diffusional restrictions imposed on the glutathionyl radicals formed after the homolytic cleavage of the S-N bond, impeding the dimerization reaction and favouring the recombination between the glutathionyl and NO radicals.

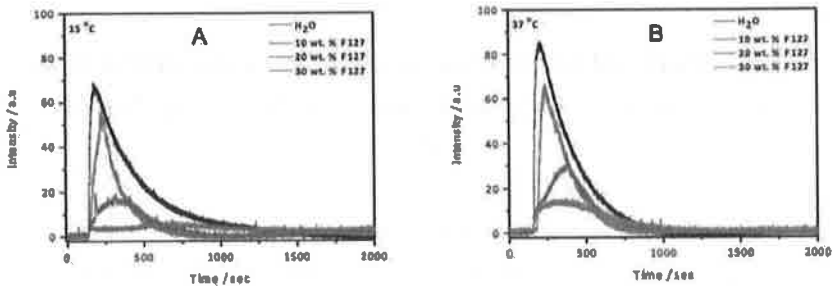


Figure 1. (A) Real time photochemical nitric oxide (NO) release from S-nitrosoglutathione (GSNO) dissolved in F127 solutions 10 wt%, 20wt% and 30 wt% at 15°C (A) and 30 °C (B).

Photochemical nitric oxide release from sno-containing poly(vinyl alcohol) membranes for increasing dermal vasodilation

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Nitric oxide (NO) is an endogenously found radical species, which plays important roles in many physiological processes, including the control of vascular tone. Microcirculatory disorders associated with the depletion of endogenous NO production are the underlying causes of ischemic diseases and chronic wounds and have demanded biomaterials capable of delivering NO locally to tissues in a controlled manner. In this work, we used mercaptosuccinic acid (MSA) to prepare SH-containing, crosslinked poly(vinyl alcohol) membranes (PVA-SH) via esterification reaction. The membranes were cast by precipitation of the polymeric solutions through their immersion in acetone, washed with water and acetone, dried by lyophilization and subsequently S-nitrosated with nitrous acid, yielding PVA-SNO membranes. Real time chemiluminescence measurements (NOA Sievers 280i, CO, USA) showed that the PVA-SNO membranes are capable of releasing NO thermally and that their irradiation with visible light from a LED source (LMI-6000 LED Fiber optic, 780 lumens, MS, USA) leads to a ca. 10-fold increase in the first order rate constant of NO release. This increase was reflected in a more intense skin vasodilation (measured by laser Doppler flowmetry) and erythema formation in the forearm of health volunteers, when compared with the topical application of the PVA-SNO membranes in the absence of light. These results show that irradiation of topically applied PVA-SNO membranes can be used as a tool to modulate the rate of NO release and the skin vasodilation in the topical treatment of ischemic skin diseases.

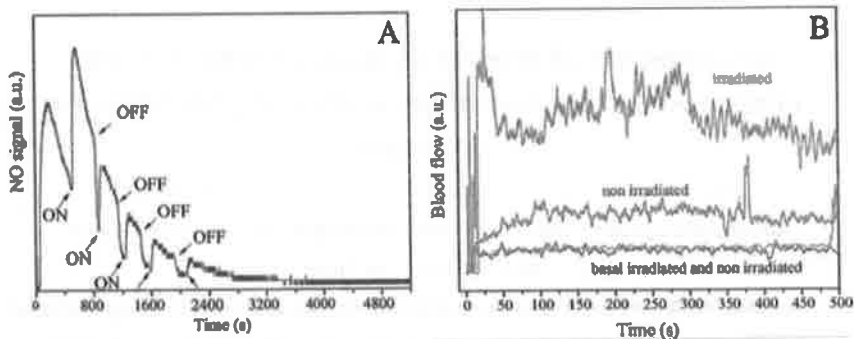


Figure 1. (A) Real time NO release from a PVA-SNO membrane showing the increase in the amount of NO released after switching on the lamp. Switching off the lamp, reduces the amount of NO released. (B) Dermal microcirculatory blood flow increase after topical application of PVA-SNO membranes. The vasodilator effect caused by irradiated PVA-SNO membranes is higher, compared with the non-irradiated membranes.

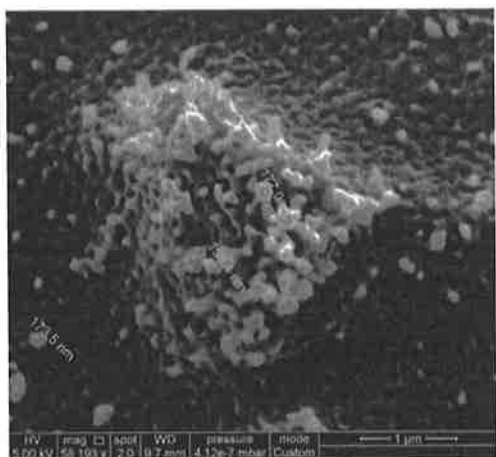
Development of innovative photosensitizer loaded nanostructured formulations applied to photodynamic processes

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Photodynamic Therapy (PDT) is based on photo-oxidative reactions, in which a photosensitizer (PS) is excited by visible light to promote irreversible destruction of tumor tissue. The second-generation PS aluminum phthalocyanine chloride (AlCIPc) was chosen owing to its strong absorption band in the 650 nm region of the electromagnetic spectrum transparent to the skin tissue and useful in the treatment of tumors. However, to overcome AlCIPc's high lipophilicity to reach a feasible administration, changes are required on PS structure or its incorporation into nanosystems. The system so called catanionic vesicles (VesCat) comprises self-assembly unilamellar vesicles spontaneously obtained mixing oppositely charged surfactants. In this work, a process of optimization was done following a protocol already described to obtain the vesicles from a tricatenaar catanionic surfactant (TriCat), saving 55% of the production time. The parameters changed did not affect the stability of VesCat/AlCIPc, with mean diameter 275 nm (obtained by PCS), polydispersity index of 0,38 and zeta potential -24 mV. Encapsulation efficiency feature of approximately 100% of AlCIPc is in agreement with the expected since AlCIPc is extremely hydrophobic. The stability of the samples kept at 4°C and at room temperature (25°C) showed no significant difference during 4 days. However, significant changes were observed within the first 24 h analysis at 37°C, with an increase of 60% for size, 35% for Pdl and after 48 h, the variation of both parameters was 200% higher. Images of the colloidal system obtained by scanning electron microscopy after freeze-fracture of the sample (Figure 1) showed homogeneous appearance with predominantly spherical and rounded aggregates. So, this analyze provides images to prove the nanostructures formation, with size according to the results obtained by PCS. Therefore, catanionic vesicles consist of a stable, compatible and nanometric system, suitable to be used in PDT.



Investigation of structural and dynamic properties of *P. fluorescens* in aqueous and organic solvents by fluorescence correlation spectroscopy

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The study of structural stability and activity of enzymes in aqueous and organic solvents has been made for several research groups from different areas. In biocatalysis, the use of organic solvents is especially advantageous in conversion of unstable substrates or poorly soluble in water. However, the exposure of enzymes to organic solvents is related to diffusional limitations, high saturating substrate concentrations, restricted protein flexibility and low stabilization of the enzyme–substrate intermediate. Fluorescence correlation spectroscopy (FCS) has been applied to study proteins, lipids, vesicles and biological cells. Here, we use FCS measurements to study structural and dynamic properties of the lipase Amano AK from *Pseudomonas fluorescens* in aqueous [phosphate buffer, pH 7.0 (0.1 mol.L⁻¹)] and organic solvents (chloroform, toluene, ethyl acetate, acetonitrile and hexane). Diffusion coefficients, concentrations and hydrodynamic radii properties were obtained. The diffusion coefficients of the enzyme dissolved in different solvents showed similar values, ranging from 506.7 $\mu\text{m}^2\cdot\text{s}^{-1}$ to 447.1 $\mu\text{m}^2\cdot\text{s}^{-1}$, except for toluene, which showed the lowest diffusion coefficient, 316.4 $\mu\text{m}^2\cdot\text{s}^{-1}$, probably due to its high viscosity (0.56 mPa.s). When the enzyme was dissolved in aqueous phosphate buffer, it revealed a unique behavior. Its autocorrelation curve only could be fitted by 2 components with distinct diffusion coefficients, 373.1 $\mu\text{m}^2\cdot\text{s}^{-1}$ and 28.9 $\mu\text{m}^2\cdot\text{s}^{-1}$. Analyzing the concentration of the enzyme in different solvents, the partition coefficient (log P) and the concentration of the lipase were inversely proportional. Another parameter investigated was the hydrodynamic radius, which is intimately linked to enzyme structure and polarity. The radius of lipase from *P. fluorescens* showed a similar behavior in organic solvents when compared to the aqueous buffer.

Synthesis and photophysics of bisazopyrroles derivatives

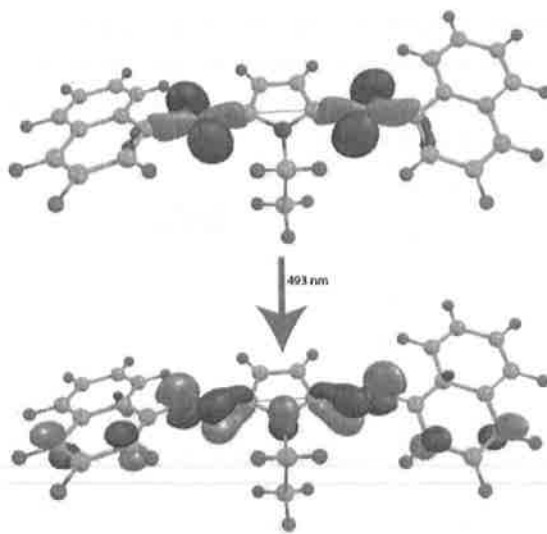
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Chromophores like azopyrroles have recently studied for their optical, electrochemical and energy harvesting properties, due to their big aromaticity of pyrrole and relatively easy synthesis of azo derivatives, they've been using in organic solar cells and studied their optical properties and molecular distribution to enhance their donor-acceptor properties for organic electronics. We have undertaken DFT and TDDFT calculation and Frontier Molecular Orbitals (FMO) analysis for design new azopyrroles compounds like small molecule organic semiconductors. The Band Gap was analysed in ground and excited state looking the probability transition in molecular orbitals to enhance transitions of $\pi-\pi^*$ and $n-\pi^*$. These derivatives were synthesized and their optical properties were analysed to obtain molecules with band gaps between 1.7 and 2.3.

Acknowledgements

The authors are grateful for the financial support of Universidad Nacional de Colombia, DIME project 20101008123.

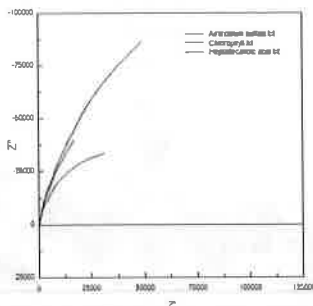


Effect of different assembly parameters in the adsorption of natural dyes in dssc

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Dye sensitized solar cells (DSSC) are photoelectrochemical devices that resemble natural photosynthesis, because they use an organic dye to absorb light and produce a flow of electrons. Today, many researches are conducting around the search of the best dye in order to improve energy efficiency conversion. The use of natural dyes is an attractive alternative due to the low cost of fabrication and the environmental benefits related to their employment. Phycocyanin, a blue protein, 36 kDa, shows promising spectroscopic and electrochemical characteristics that made it suitable for its use in the DSSC. The dye also contains a chromophore with carboxylic moieties to establish bonds with the TiO_2 . However, when the cell is assembled, very low efficiency values arising from a poor adsorption of the dye to the TiO_2 modified electrode can be detected. For that reason, we carried out electrochemical impedance spectroscopy studies of the cells to evaluate how different assembly parameters affect the amount of the natural dye adsorbed onto the semiconductor. The use of additive co-adsorbents is a key point for the preparation of DSSC; ammonium sulfate, chlorophyll and fatty acids were studied in this work. Additionally, pH measurement represents another important condition due to the fact that the protein structure depends of the chemical environment of the solution.



Solid lipid nanoparticles as drug delivery system for photosensitizers applied to photodynamic therapy

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Photodynamic Therapy (PDT) is a novel effective treatment of cancer and non-oncological skin diseases. This minimally invasive procedure requires application of a photosensitizer (PS) followed by its activation with visible light at an appropriate wavelength, in the presence of oxygen, that generate reactive oxygen species involved in subsequent biochemical events resulting in cell death. Aluminum phthalocyanine chloride (AlClPc) was chosen as a PS. This second generation compounds is very efficient, but its high hydrophobicity makes necessary changes on structure or development of DDS (drug delivery system) for its administration. The aim of this study was to develop stable Solid lipid Nanoparticles (SLN) allowing the application of AlClPc in PDT. SLN where produced by phase inversion methodology. It was composed by Compritol 888ATO (solid lipid), the surfactants PEG-40 Hydrogenated Castor Oil and Sorbitan Isostearate in ultrapure water. SLN empty and AlClPc-loaded with 7 different concentration in the range 0.05-0.4 mg ml⁻¹ were studied. They presented mean diameter between 120.4-179.7 nm, low polydispersity index (0.188 e 0.302) and zeta potential between -23.6 e -34.1 mV with bench stability for at least 4 months. The studies using forced stability test with

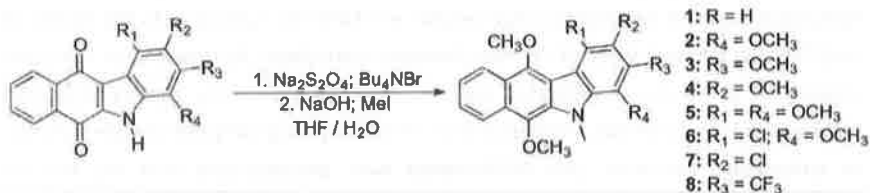
Lumisizer equipment revealed that SLN samples are stable for a period up to 7.0 months of shelf life. The spherical shape of the nanostructures were shown by transmission electronic microscopy, which also corroborated with the mean diameter of the nanoparticles. XRD measurements confirmed the integration of the PS in the lipid crystal lattice with the presence of polymorphic structures. SLN AlClPc-loaded were biocompatible with the NIH-3T3 fibroblasts cell line between 0.39-0.1 µg ml⁻¹. Hence, the SLN developed in this work are stable and can be used as drug carriers for AlClPc, providing an excellent alternative to be applied in PDT.

Photophysical characterization of substituted methyl benzocarbazolediol ethers

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A series of methyl benzocarbazolediol ethers were prepared by reduction/methylation reactions of the respective 1,4-quinones (Esquema 1). Due to the intense fluorescence of the benzocarbazolediol ethers, the compounds were photophysically studied in order to characterize them for future biological and technological applications. The absorption and emission spectra were recorded in solvents of different polarity: cyclohexane, dichloromethane, and methanol. The absorption spectra for all compounds show intense bands at 275 - 315 nm (for example 1 in acetonitrile $\lambda = 275$ nm, $\epsilon_{\text{max}} \sim 48700$ L.mol⁻¹cm⁻¹) and a less intense band 400 - 450nm (for 1 in acetonitrile $\lambda = 386$ nm, $\epsilon_{\text{max}} \sim 3600$ L.mol⁻¹cm⁻¹). No solvatochromic effect on the absorption spectra of the compounds was observed. The fluorescence emission spectra occur in the range of 400-500 nm and reveal a solvatochromic red shift in acetonitrile ($\Delta 10$ nm for 1 compared with cyclohexane as solvent). The fluorescence quantum yield of these compounds were determined using the comparative method (perylene as standard, $\Phi_f = 0.94$ in cyclohexane)¹ and were found to vary in the range 0.3 - 0.6 in cyclohexane with the exception of the chlorinated compounds 6 and 7 which showed reduced fluorescence quantum yields ($\Phi_f = 0.1 - 0.2$). Similar values were observed using the other solvents. These results can be compared to those obtained for carbazole, which has a similar structure and for which $\Phi_f = 0.5$ in a mixture of diethyl ether, pentane and methanol 5:5:2.2 ¹Brouwer, A.M.; Pure Appl. Chem. 2011, 83 (12), 2213. ²Adams, J.E.; Mantulin, W.W.; Huber, J.R.; J. American Chemical Society 1973; 95 (17), 5477.



Scheme 1

Inactivation of tyrosinase photoinduced by carboxypterin under solar radiation

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UV-A radiation can induce damage to biomacromolecules through photosensitized reactions. This indirect action may be mediated by endogenous or exogenous photosensitizers and can take place via different mechanisms. The melanin of the epidermis is the main protection against the harmful effects of UV solar radiation. Tyrosinase is a glycoprotein that, in mammals, catalyzes the rate-limiting step in the synthesis of melanin. Vitiligo is a skin disease that causes lack of pigmentation due to inactivation of enzymes of the melanogenesis. In diseased skin cells micromolar concentration of pterin derivatives such as carboxypterin (Cap) have been determined [1]. A recent study has demonstrated that under UV-A radiation, tyrosinase is inactivated by pterin through a photosensitized process [2]. Moreover, aqueous solutions of pterin derivatives suffer photooxidation under solar exposure and outdoor conditions [3]. Taking into account that UV light reaches the epidermis, where pterins derivatives are present in some pathological conditions such as vitiligo, the main aim of this work is to find out if the energy of the sun is enough to cause photoinduced inactivation of tyrosinase using Cap as photosensitizer. Aqueous solutions containing the enzyme and the photosensitizer were exposed to sunlight and analyzed by UV-Vis spectrophotometry, enzyme activity measurement, fluorescence spectroscopy, electrophoresis (SDS-PAGE) and HPLC. The results indicated that Cap can photoinactivate the tyrosinase under solar radiation. Upon irradiation tyrosinase structure and tryptophan residues were altered. [1] K.U. Schallreuter, et. al., *Science*, 1994, 263, 1444. [2] M. L.Dántola, et. al., *Biochem. Biophys. Res. Commun.*, 2012, 424, 568. [3] A. Ipiña, et. al., *Solar Energy*, 2014, 109, 45.

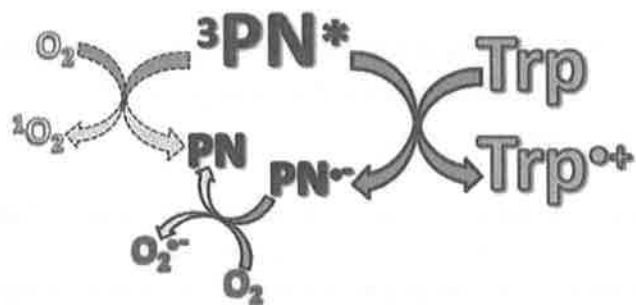
A non-singlet oxygen mediated reaction photoinduced by phenalenone, a universal reference for singlet oxygen sensitization

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Although photosensitized oxidations may involve the generation of radicals (type I mechanism) and/or the production of singlet molecular oxygen (1O_2) (type II mechanism), it is generally accepted that the photosensitization of proteins occurs mainly through the reactions of 1O_2 with tryptophan (Trp) and other amino acids. In this work, we have investigated the mechanism of the oxidation of Trp photosensitized by phenalenone, one of the well-known type II photosensitizers, widely used as a 1O_2 reference sensitizer. From the results obtained, it could be established that 1O_2 played a minor role and that the predominant mechanism of the photosensitization of Trp by PN involved an electron transfer process (type I mechanism). The mechanism proposed is summarized as follows. After UV-A excitation of PN and formation of its triplet excited state ($^3PN^{**}$), three reaction pathways compete for the deactivation of the latter: intersystem crossing to singlet ground state, energy transfer to O_2 leading to the regeneration of P_{tr} and the production of 1O_2 , and electron transfer between Trp and $^3PN^*$ yielding the corresponding pair of radical ions ($PN^{\bullet-}$ and $Trp^{\bullet+}$). In the following step, the electron transfer from $PN^{\bullet-}$ to O_2 regenerates PN and forms $O_2^{\bullet-}$. Finally, the reaction of $Trp^{\bullet+}/Trp(-H)^{\bullet}$ with O_2 leads to the formation of products. In the absence of O_2 recombination of $PN^{\bullet-}$ and $Trp^{\bullet+}$ recovers the reactants and, therefore no consumption of the amino acid is observed under anaerobic conditions. These findings call into question the role of 1O_2 in processes involved in the photodynamic effects of a variety of photosensitizers in living systems.

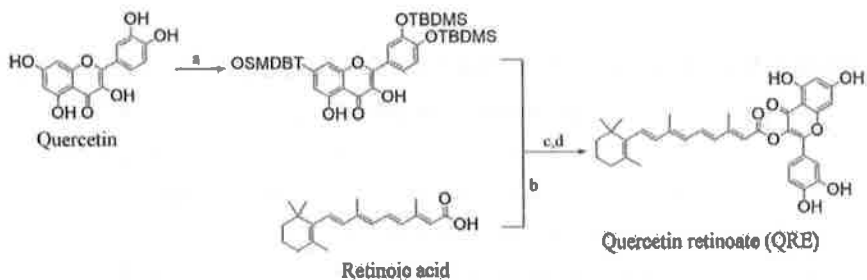


Quercetin-3'-retinoate a new photoprotective bifunctional antioxidant with enhanced properties.

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Plant phenols are ubiquitous in the plant kingdom and generally involved in the defence against UV radiation, mechanical injury and aggression by pathogens. Increasing attention in the last decade has growth in the potential health benefits of dietary plant phenols as natural antioxidants. Recently, we show that esterification of ferulic acid with astaxanthin simultaneously improves the antioxidant activity of the plant phenol and the carotenoid moiety in the newly synthesized antioxidant, astaxanthin diferulate, to become a bifunctional antioxidant with enhanced activity. The potential of such bifunctional molecules simultaneously functioning as antireductants and as antioxidants is completely unexplored and deserves attention both in relation to singlet oxygen quenching and electron transfer processes. In this direction, herein, we report the synthesis, photophysical characterization, singlet oxygen quenching, and photoreaction with triplet-safranin of the newly synthesized bifunctional antioxidant, quercetin-3'-retinoate (QRE). Quercetin (QE) and retinoic acid (RA) shown high rate constant for chemical quenching of singlet-oxygen ($>10^9 \text{ M}^{-1}\text{s}^{-1}$), however, QRE did not show any reactivity towards singlet-oxygen. After excitation of QRE solution at 266 nm, laser flash photolysis experiments suggest the formation of a long-lived radical species ($> 10 \text{ ms}$) at 420 nm, indicating an instable reagent molecule in the excited-state, which is not observed for the precursors. In the presence of photoexcited safranin, as probe molecule for electron transfer processes, the T-T band of safranin is shown to be quenched by QRE yielding the semi-reduced radical species of safranin with absorption maximum centered at 650 with $k_q = 10^9 \text{ M}^{-1}\text{s}^{-1}$, similar to the precursors. In fact, the lack of chemical with photochemical generated singlet-oxygen and its high antioxidant activity, suggest QRE as a promisor chemopreventive antioxidant for food and biological purposes.



Photoliziation



Photosensitization



Photodegradation of 3,5-dinitrosalicylic acid by uv photolysis of hydrogen peroxide

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The goal of this work was to evaluate the degradation of 3,5-dinitrosalicylic acid (DNS) by homogeneous photochemical Advanced Oxidation Process (AOP). The DNS method is used to determine the concentration of reducing sugars in biomass hydrolysates¹. Research laboratories and undergraduate biochemistry courses of the Department of Chemistry of the University of Sao Paulo largely use this method. However, due to its toxicity, it is not recommended the direct disposal of DNS into the sewer, transforming it in a potential wastewater residue. Every semester, the Department of Chemistry generates ca. of 20 L of this waste, which is kept in storage rooms. For this reason, we have used the UV photolysis of hydrogen peroxide² for the photochemical degradation of the DNS. As there is a lack of information about the DNS in literature, we have started our studies determining the pKa of DNS by potentiometric titration. The pK₁ and pK₂ are respectively, 2.1 and 7.2. The nitro groups present at the structure, decrease the pKa of the salicylic acid (3.0 and 13.4)³. Based on these values, aqueous solution of DNS 1.0 mmol/L at three pHs (2; 6, and 12) adjusted with an aqueous solution of sodium hydroxide 1.0 mol/L, were used for the photodegradation studies. The photodegradation was performed in a photochemical reactor using a mercury vapour lamp without the bulb (125 W, H1A016, Sylvania). After we turned the lamp on, there was a continuous addition of hydrogen peroxide with a flow of 0.15 mL/min. Periodically, 10 mL aliquots were taken for UV/visible absorption measurements. The total organic carbon (TOC) were also measured in TOC Shimadzu Control V – CPH/CPN analyser.

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Acknowledgements

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Photoluminescent silicon nanoparticles

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Porous silicon nanoparticles have shown autofluorescence and biocompatibility in vitro studies. The fluorescence emission of this material in the phototherapeutic window region are interesting for its application for photodiagnostic visualization in vitro and in vivo studies. The isolation of nanoparticles with monodisperse size and discreet emission peak represents great challenges. This work reports the synthesis, characterization and application silicon nanoparticles in vitro studies. An electrochemical cell and a hydrofluoric acid electrolyte solutions were used to obtain porous silicon nanoparticles from p-type crystalline silicon substrates. The use of fluorescence spectroscopy, dynamic light scattering, SEM and X-ray diffraction allowed its characterization. Cell viability assays by the MTT method allowed us to evaluate its biocompatibility. In this sense, controlling electrochemical parameters allowed to obtain silicon nanoparticles with good optical properties and high purity level. Fluorescence measurements have revealed the capacity of emission in a wide range of the electromagnetic spectrum from UV to near infrared. Cytotoxicity assays using murine melanoma cells line, as a model, has demonstrated the biocompatibility of this material in vitro assays. The H-NMR analysis showed that the silicon nanoparticles have an effective chemical interaction with oligopeptides with antitumor activity. These results have shown that the electrochemical method is low cost methods that allow obtaining silicon nanoparticles with chemical and optical properties suitable for functionalization with molecules with antitumor activity targeting their application in cancer treatment.

Development and characterization of hydrogel nanocarrier to skin release of chlorine aluminium phthalocyanine and methylene blue photosensitizers

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In Brazil, skin cancer is the most common form of the disease, and related at 25% of all malignant tumours registered in the country. It has high rates of cure if detected early. The most common types are basal cell carcinomas, which accounts for 70% of diagnoses, and squamous cell carcinomas, representing 25% of cases. Basal cell carcinoma, although more common, it is also the least aggressive. Thus, our work aims to develop and characterize a thermos-sensitive hydrogels carried out by poloxamer ultra-homogenization, and association of chlorine aluminium phthalocyanine (AIClPc) and methylene blue (MB) photosensitizers, as described by SELLERS et al. 2014. This nanomaterial is a topical drug delivery system for release of photosensitizers compounds for use in photodiagnostic and skin cancer treatment. The results showed a particle size of 180.1 nm (± 0.9), a zeta potential of -13.5 mV (± 1.3), and polydispersity index (Pdl) of 0.8 (± 0.1). The combination of active AIClPc associated with the MB did not alter the steady-state and photophysical properties of both, keeping its profile absorbance and emission at 682 nm and 664 nm to AIClPc and MB respectively. The initial proposal for the development and characterization of hydrogels containing AIClPc associated with the AM was accomplished; it is possible to achieve a stable and nanotechnological material. In vitro studies were performed to evaluate the biological compatibility of the nanomaterial after incubation during 3 hours on monolayer cell culture of human gingival fibroblasts. In vitro assays demonstrated the AIClPc/nanogel has appropriate biocompatible to concentration of 16.2 $\mu\text{mol.L}^{-1}$. In the future, additional studies will be evaluate the potential of this nanomaterial, based in preclinical studies to photodiagnostic proceeding, skin cancer treatment and also to infectious processes control in the post-operative wound healing of head and neck surgery, based Photodynamic Therapy.

Activity nanocapsules containing aluminum phthalocyanine chloride associated with leishmanicidal drugs based photodynamic therapy

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Leishmaniasis is a neglected tropical disease caused by the protozoan *Leishmania*. Conventional drugs used today to treat are toxic, expensive and require long periods of therapy. This work proposed the use of photodynamic therapy (PDT) with aluminum chloride phthalocyanine (AlClPc) associated with antileishmanial drugs (resveratrol, amphotericin B and chalcone CH8) encapsulated in polymeric nanocapsules. We evaluated its phototoxic effects on macrophage lineage RAW 264.7. The loaded nanocapsules were prepared by nanoprecipitation method and characterized by particle size, poly dispersion index, zeta potential, encapsulation efficiency and spectroscopic analysis. The nanocapsules had an average diameter of 230 nm, low polydispersity (0.3) and a negative zeta potential (approximately -30 mV). The spectroscopic properties (absorption and fluorescence) of AlClPc present the same behavior without or in association with the antileishmanial drugs. The encapsulation efficiency of the aluminum phthalocyanine chloride was around 75%, as expected for hydrophobic drugs. Nanocapsules exhibited good physical stability over a 3 month period which was confirmed by the accelerated stability studies. The phototoxic effect caused by nanocapsules AlClPc (5 μ M), AlClPc (5 μ M)+ Resveratrol(50 μ M), AlClPc (5 μ M) + amphotericin B (4 μ M) and AlClPc (5 μ M) + chalcone (10 μ M) under irradiation light at 1 J cm⁻², (the highest dose used) showed the highest percentage of cell death up to 70% in the first two cases, 50% in the third and 90% in the last. The results of this study indicate that the polymeric nanocapsules work well as a potential drug delivery system for AlClPc alone or associated with other antileishmanial at low concentration and low dose of visible light, encouraging further studies *in vivo*.

Chloroaluminum phthalocyanine-photosensitizer conjugated with magnetic-nanoemulsion for photodynamic/photothermal therapy in stem cells model

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During cancer treatment, therapeutic compounds often need to be delivered into individual tumor cells to exert anticancer effects. Targeted delivery of drug molecules using nanodevices can improve biodistribution and increasing efficacy and reducing side effects. Cancer stem cells (CSCs) are only a small percentage of the total cell population, CSCs are a unique subset of tumor cells thought to play a critical role in the initiation and progression of carcinogenesis. Studies suggest similarities of CD133+ CSC with the proneural subtype and of CD133 CSC with the mesenchymal subtype. Many strategies have been developed to overcome these problems. Among these, drug delivery nanosystems have been produced to target therapeutic agents and improve their biodistribution and therapeutic index in the tumor. At the same time, Photothermal (PTT) and Photodynamic therapy (PDT) is a promising treatment for a variety of oncological diseases. In this study we developed an innovative magnetic-nanoemulsion (MNE) citrate functionalized loaded with chloroaluminum phthalocyanine-photosensitizer. The magnetic nanoparticles were incorporated into nanoemulsion using a highly-stable ionic magnetic fluid in a spontaneous emulsification method. Our findings demonstrate excellent physical and chemical stability of MNE with a size less than 200 nm, exhibiting a narrow size distribution (PI index less than 0.2) and the zeta potential higher around $|40|$ mV. The in vitro studies using the human mesenchymal stem cells derived from bone marrow cell line indicate biocompatibility of MNE establishing safe drug delivery systems with drugs concentration for the specific cells types. Confocal studies clear indicate the intracellular localization and active site of the drug combination. As a result, combined PDT and PTT showed a more pronounced synergistic effect than the sum of the individual therapies. This combination has therefore become a promising paradigm for cancer

intervention. Traditionally, the combined therapy relies on two separate treatments, which have to be carefully arranged in order to achieve synchronized effects.

Photodynamic effect in medulloblastoma: regulation of epidermal growth factor pathway

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Medulloblastoma (MB) is also a malignant embryonic tumor of the cerebellum, whose incidence occurs preferentially in children under 7 years. Brain tumors differ from between them at the molecular level. The amplification of the EGFR (Epidermal Growth Factor Receptor) gene with an increase in the expression of EGFR is the main cause in is also present in medulloblastoma. In this study, we developed nanoemulsion (NE) citrate functionalized loaded with photosensitizers compound as a chloroaluminum phthalocyanine (CIAIPc) molecules. Our findings demonstrate excellent physical and chemical stability of NE with a size less than 200 nm, exhibiting a narrow size distribution (PI index less than 0.2) and the zeta potential higher around $|40|$ mV. The in vitro studies using the cell line of MB indicate biocompatibility of NE establishing safe drug delivery systems with drugs concentration to 0.5 mg/mL of CIAIPc for the specific cell type treated by photodynamic therapy (PDT). PDT's share knowledge in brain tumors at the molecular level allowed to discovery of genes that participate in the regulation of gene expression of other RTK/Ras/PI3-K and AKT/MAPK signaling pathways such as that are responsible for the increased cell proliferation, survival or resistance to apoptosis and loss of adhesion and migration, and may reveal a high degree of invasiveness. For this reason, treatment with photodynamic therapy in brain tumor cells adds relevant information about the process of cellular proliferation and cancer biology.

Experimental setup for simultaneous measurement of electrical and optical properties of semiconducting polymer devices

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Conjugated polymers have been object of intense study in the last two decades. Due to their optical and electrical properties, they can potentially substitute inorganic materials as active layer in displays and photovoltaic cells. However some aspects prevent their commercial use. Polymer light emitting diode lifetime and efficiency are still low and are determined by photochemistry processes, as photooxidation, by structural properties, as chain conformation, as well as by the polymer electronic structure. We describe an experimental setup based on commercial instruments that allows simultaneous measurement of the current-voltage curve, electroluminescence, luminance, and chromaticity of polymer devices. A Keithley sourcemeter instrument applies a voltage ramp to the device electrodes in determined voltage steps, and measure the current through the device. At each step, an USB Ocean Optics spectrometer measures the electroluminescence spectrum, and a Konica Minolta chromameter measures the luminance and the chromaticity. The experimental setup is controlled by a laptop with a program developed in LabVIEW. The experimental data provides a complete set of information relating the spectral and optical changes with the electrical behavior during the characterization of the polymer diode.

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Synthesis and characterization of new luminescent Tb(III) complex by the application of ugi multicomponent reaction (mcr) on a tröger's bases scaffold

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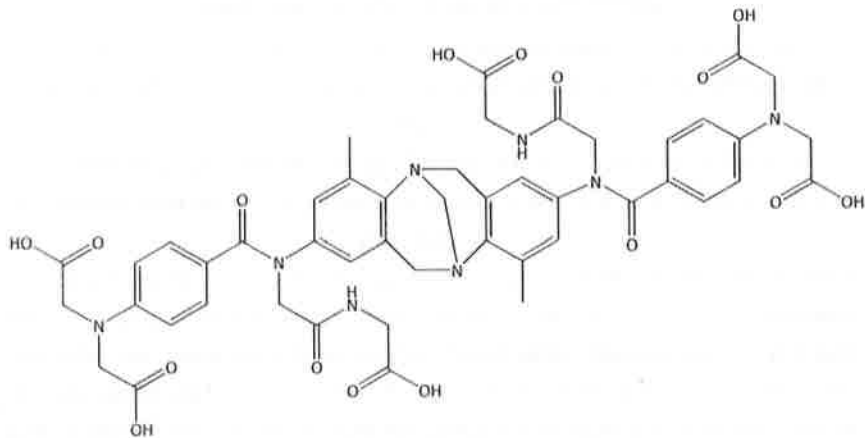
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Research in the area of luminescent lanthanide complexes is in constant growth, thanks to its applications in various fields such as sensors, light emitting devices, etc.[1] Due to the extremely low light absorption of lanthanides it is essential to find ligands that allow both metal complexation and its sensitization, and which in turn can be suitably functionalized to be used in the desired applications. It is known that MCRs are an effective synthetic strategy in the construction of compound libraries, and in this sense the Ugi MCR can be used for simultaneous introduction of several coordinating groups and/or chromophores into a selected scaffold, and would thus be an extraordinary methodology for the synthesis of this kind of complexes. One structure around which we can build a unique architecture in this area is the Tröger's base, its "V" shape allows placing different functional groups, with remote connectivity but close in space [2]. Polycarboxylic acid **1** was synthesized in eight steps from simple precursors, with an Ugi MCR as the key step. **1** was characterized by 1D and 2D NMR, MS and by IR spectroscopy, and with its UV-vis absorption and emission/excitation spectra. The formation of the Tb (III) complex of **1** and its sensitization was evident through the excitation and emission spectra, in which the characteristic narrow bands of terbium emission, were observed. The formation of a 1:1 stoichiometry complex was confirmed using the most intense emission at 545 nm through Job's plots and by titration of **1** with Tb (III). In the same way the formation of a 1:1 complex between 1:1 Eu (III) and **1** was also established. In summary, in this first stage of labor we synthesized and characterized a new ligand capable of forming complexes with Tb and Eu using an Ugi MCR.

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1: Polycarboxylic acid derivative of Troger's base.

Degradation mechanism of purine nucleotides photosensitized by pterin: a radical charge transfer model

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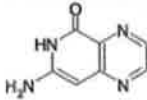
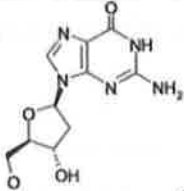
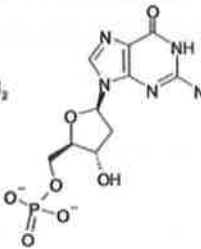
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Pterins belong to a family of heterocyclic compounds present in a wide range of living systems and participate in relevant biological functions. Under UV-A excitation (320–400 nm), pterins can fluoresce, undergo photooxidation and generate reactive oxygen species (ROS) [1]. In the presence of oxygen, pterin (Ptr) act as photosensitizer through type I and/or type II mechanisms [2-3]. The photosensitized degradations of the guanine nucleotide and nucleoside, dGMP and dG respectively, by Ptr were studied in neutral aqueous solutions upon UV-A irradiation (350 nm).

Photophysical properties of the triplet excited states of the sensitizer and the radical species formed in the process were characterized using laser flash photolysis. After analysis of the results, the mechanisms were proposed. Under anaerobic conditions, a recombination of the radicals occurred, and no consumption of the substrate (S, being S dGMP or dG, depending on the experiment) was registered. In the presence of O₂, it was observed more consumption of dGMP or dG than saturated O₂ solutions. In this case, there exist a competition between different reactions that includes type I and type II mechanisms for guanine. The main reaction is initiated by an electron transfer from the substrate to the triplet excited state of Ptr yielding the corresponding pair of radical ions (Ptr^{•-} and S^{•+}), with subsequent recovery of the photosensitizer by electron transfer from Ptr^{•-} to O₂. Finally, the substrate radical participates in later reactions to yield degradation products. Although the reaction between the guanine and ¹O₂ takes place, does not contribute significantly to the substrate consumption.

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Sensitizer	Substrates (S)	
		
Pterin (Ptr)	2'-deoxyadenosine 5'-monophosphate (dG)	2'-deoxyguanosine 5'-monophosphate (dGMP)

Chloroaluminum phthalocyanine loaded with cholesterol rich nanoemulsion mediated photodynamic therapy of human glioblastoma cancer

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Malignant gliomas are the most common brain tumor type, occurring in 5-7 per 100,000 individuals per year. This tumor type is characterized by a fast aggressive growing and by the ability to infiltrate the surrounding healthy brain tissue, which is always associated with a poor prognosis. Photodynamic therapy (PDT) has been emerging as an alternative for the treatment of brain tumors, and has shown promising results, both in vitro and in vivo, is a simple and non-invasive technique. The main purpose of the present study was to determine the efficacy of PDT using free Chloroaluminum phthalocyanine (PcAICl) encapsulated in a cholesterol-rich nanoemulsion (NEPc). MTT assays were performed to evaluate the mitochondrial activity of U87MG cells after 24h of incubation for 3h with PcAICl or NEPc at concentration of 0.25 μ M, treated with visible light. The Laser irradiation used was setup at 660nm with fluency range from 40mJ to 1J in a continuous wave mode. From the data obtained mitochondrial activity was estimated by classical MTT assay in the dark and in PDT treatments. The results demonstrated no cytotoxicity in the range of 0.25 to 1 μ M in the dark for PcAICl and NEPc. After Laser irradiation of control group no changes in the cellular viability were observed. Meanwhile, there was a significant decrease in the viability after 24h post-irradiation with free PcAICl and NEPc to all light doses used, whereas, the light dose which showed the best activity was 1J. At this light dose, the cell viability decreased 18% for PcAICl and 50% for NEPc. These results indicate that the NEPc showed an increased in the PDT activity when compared to free PcAICl as expected. These results reinforce the idea that the use of cholesterol-rich nanoemulsion as drug delivery system for PcAICl is useful for PDT of brain cancer cells.

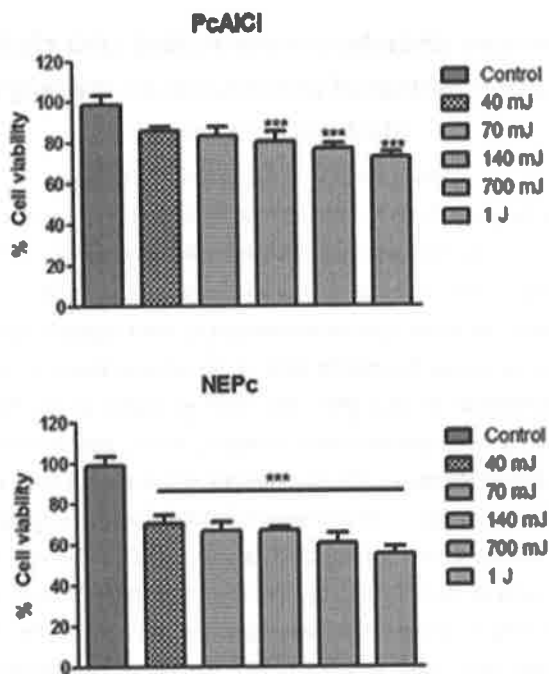


Figure 1: U87MG cells incubated with $0.25\mu\text{M}$ of PcAlCl or NEPc for 3h and then irradiated with different light doses. Analysis of variance (ANOVA) showed that the differences among the light doses were significant ($p < 0.05$) in relation to the control. Data are expressed as mean \pm SD ($n=3$)

Study of diffusion during radical polymerization of styrene: direct determination of translational motion by single molecule spectroscopy

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Investigation of diffusion properties of polymer systems plays a pivotal role in the understanding of rheological parameters, and consequently in polymer processing and assembly of plastics, films, and fibers. In the last years, different groups have been studying dynamic processes at single molecule level by the use of dye molecules as probes. However, it represents an indirect way to determine diffusion motion into the polymer. Here we use fluorescence correlation spectroscopy (FCS) and wide field microscopy (WFM) to follow changes in diffusion coefficient of polymer chains during polymerization processes. The use of linear and star-shaped alkoxyamine-based initiators, containing the dye perylene diimide attached in their structures allowed us to show the development of heterogeneities of the chain movement into the polymer network, by direct measurements. Bulk polymerization mediated by linear initiators show slower monomer conversion, when compared to star-shaped polymerization. Whereas starshaped polystyrene shows narrow step-length distribution and low values of MSD ($0.055 \text{ } \mu\text{m}^2$ after 0.8 s) after 180 min, linear polystyrene, labelled by linear and star-shaped fluorescent polymer chains, present broad range of step-length distribution, similar values for conversion evolution and MSD. Therefore, during the polymerization progress, changes in viscosity represent the main role in the pattern of diffusion parameters. In summary, the direct investigation of heterogeneities of dynamic properties related to different polymer matrices by single-molecule techniques, FCS and WFM represent a powerful tool to unravel information that could be hidden in observations performed by indirect probes. By the application of this deep knowledge about heterogeneities of molecular motion, it is possible to produce polymers with well controlled structures.

Organic condensation reaction with nanoparticle catalysis accompanied at the single molecule level by fluorescence microscopy

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Macroscopic kinetic studies are usually conducted with a large number of molecules, generating information about catalytic average rate, substrate specificity, among others. However, these data do not reveal properties of individual molecules which can vary considerably. Nevertheless, single molecule techniques can lead to unexpected observation fluctuations, such as oscillations or stochastic behavior. It's possible to obtain information about the effective contribution of each species in the overall kinetics. The environment in which the molecule is inserted also changes its physical and chemical properties and this influence can be better understood by studying only one molecule. Single-molecule fluorescence microscopy is currently one of the most powerful methods in the single-molecule toolbox because it can provide information about the real-time distribution of chemical reactivity, with high-sensitivity and high-resolution. This study objective was to follow an organic reaction with heterogeneous catalysis forming a fluorophore at the level of a few molecules in order to obtain information about the kinetics of the process. For catalyzing the reaction of magnesium oxide nanoparticles were prepared from NaOH and Mg(NO₃)₂·9H₂O and calcined at 800 ° C for 5 hours. The obtained structures, about 50 nm and strong basic character were used as catalyst for the condensation reaction of 4-(Diphenylamino) benzaldehyde with (1-phenylethylidene) propanedinitrile in ethanol to give 4- [4- (1,1- dicyano-2-phenyl) buta-1,3-dienyl] tri-phenylamine, a fluorescent dye product with maximum absorption at 490 nm. The forming process was monitored in situ at single molecule level by widefield fluorescence microscope with excitation at 473 nm using super-resolution techniques. Therefore, we studied the kinetics of catalysis dynamics in space and time, and through the emission spots observed in the oxide surface was possible to map its structure.

Electroluminescent properties of pvk:zn(ii) coordination compounds composites: tuning color from blue to near white emission

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Organic light emitting diodes (OLEDs) have attracted attention due to their promising applications in displays and solid state lighting. Current manufacturing technologies for OLEDs using small molecules involve the use of expensive high vacuum techniques and it needs thermally stable materials¹. These problems disappear when the OLED films are deposited from solution. This study aims at the production of OLEDs using as emitting layers composites of conjugated polymers (as host) and organic molecules (as guest), as an attempt to use the strategy of small molecules deposited by solution. We synthesized organic molecules and characterize them by photophysics techniques and then examined the best proportions (formation of composites) of the active layer. Zn(II) coordination compounds and their ligands were used as organic molecules and polyvinylcarbazole (PVK) as semiconducting polymer, as both are photoluminescent. We want to ensure the highest emission efficiency with easier processing and lower cost. This system was chosen because PVK and Zn(II) coordination compounds have, according to absorption/emission, spectral complementarity and can act as a host-guest system. The OLEDs were made using the compound KG15-Zn, KN10-Zn, KN10 and PVK (2,5% mol/mol), using the following configuration: ITO/PEDOT:PSS/PVK:compound/Ca/Al. The Jvs.V curves, CIE chromaticity coordinates and EL spectra will be present. Finally, the best results were obtained from the coordination compounds compared with free ligand and pure PVK polymer host.

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Correlations between Förster resonant energy transfer (FRET) and electroluminescent properties in poly-n-vinylcarbazole:[Zn(II) coordination compounds] composites

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In the present work we report the photochemical and photophysical properties of four Zn(II) coordination compounds and their ligands in DMSO solution and in solid state. Those properties were compared with Alq3 and Znq2 features. We also studied the optical properties of composites thin films of PVK and the Zn(II) compounds, Alq3 and Znq2 in steady state and dynamic conditions by electronic absorption, emission, fluorescence decays and time resolved emission spectroscopy. After optical characterization of these composites, it was constructed organic light-emitting diodes (OLEDs), and the characterization was made by L vs. V, J vs. V, chromaticity and EL spectra. The photophysical properties of the Zn(II) complexes were similar to Alq3 and Znq2: it was shown a biexponential behavior in their fluorescence decays, exhibiting absorption and emission wavelength at UV ~ blue and green ~ yellow region, respectively. Hence, those compounds have been used as energy acceptor in a host-guest system with PVK according to absorption/emission spectra complementarity, giving rise a composite that can applied as active layer in OLEDs. For PVK:[Zn(II) complexes] thin films it was observed an absorption band centered 295 nm, characteristic of PVK absorption. However in the emission spectra of composites it was observed an increase of the emission band of the coordination compounds with increasing their concentration, indicating an energy transfer between PVK and the complexes. In the fluorescence decays of composites it was observed a decrease of fluorescence lifetimes of PVK, indicating the presence of FRET in A-D system with efficiency $\approx 45\%$, according the Förster model, with saturation of FRET efficiency at 2.5% concentration. Then on OLEDs using this system, it was observed a combination of EL of PVK and Zn(II) complexes yield emission bands near to white and in green colors, increasing the optical-electronic properties of PVK when was added the coordination compounds.

Study of polyfluorene degradation applied in organic light emitting diodes (oleds) using electro and photoluminescence techniques

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Degradation studies of materials used in OLEDs are important to know in which conditions they can be stored and manipulated. This work aims to determine if there is degradation in OLEDs emissive layer, whose one of the main effects is changes in color emission. The OLEDs were made using poly[9,9-dioctylfluorenyl-2,7-diyl] (PFO) as emissive layer, which is expected to have a pure blue electroluminescence. PFO oxidation produces fluorenone which has a greenish emission at ~550nm, same region that is observed aggregates and excimers luminescence. To investigate the fluorenone presence, firstly it was acquired Carbon-13 nuclear magnetic resonance and infrared spectra of the sample, and was concluded that there was no evidence of it. Then it was obtained absorption and emission spectra, time resolved emission spectra (TRES) of PFO in thin films and in solution. Using those photoluminescence techniques it was possible to verify that the ~550nm emission band, which appears in long time in TRES only in films, can be attributed to aggregates or excimers. Finally, electroluminescence spectra of the devices, prepared and maintained during the study in argon or in open atmosphere, were obtained. The device turned-on in the presence of oxygen, the intensity of bands in green region increases with increasing voltage, while this not happens when it was used inert atmosphere. This was an evidence that the oxygen only degrades the material if there is current passing by. Recent works of single-molecular electroluminescence indicates that the ~550nm band attributed to excimers disappear in electroluminescence, so it is quite conclusive that the greenish bands who appear in open atmosphere in fact is due to fluorenone formation.

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Quenching of luminescence of tris(2,2'-bipyridine)ruthenium (ii) by a family of p-substituents of phenol

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The study of the metal complex Tris(2,2'-bipyridine)ruthenium (II) [Ru(bpy)₃+2] has been investigated extensively in the literature due to having qualities such as a strong luminescence and to being soluble in a wide variety of aqueous and non-aqueous solvents [1-3]. These properties have promoted Ru(bpy)₃+2 as one of the most used photosensitizers in the visible range. Because of this broad use, the mechanism that promotes the quenching of the excited state has been extensively studied. Particularly, quenching of the luminescence due to the reaction with phenols, whose mechanism involves a hydrogen and electron abstraction reactions [2]. Phenols are of high interest in the biological field mainly as antioxidants, photostabilizers and redox systems. However, although there are many p-derived phenols studied, to our knowledge, the range of substituents are limited in terms of electro-attractor or -donor capacity [3]. This would not allow a proper evaluation about if phenol and all the p-substituted derivatives follow a common mechanism to quenching Ru(bpy)₃+2 luminescence, or there are more than one way to make it happen. In this work results of quenching of luminescence of Ru(bpy)₃+2 due to the addition of a series of p-derivates of phenol are presented. This results show that the reaction is pH dependent, namely if the deactivating species is in a phenol or phenolate form (p-derivate). Furthermore, a comparison of the quenching constants with Hammet parameters would indicate that the mechanism of quenching involve a high degree of charge transfer.

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Ligand effect on the photophysical properties of re(i) tricarbonyl complexes

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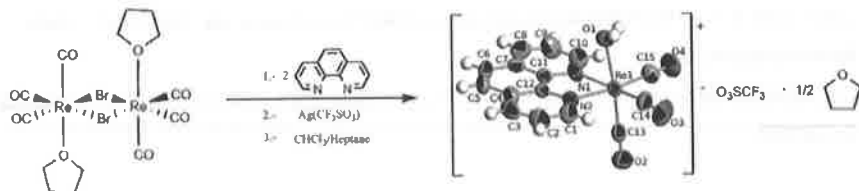
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Rhenium(I) tricarbonyl complexes, $[(N,N)Re(CO)_3(X)]$, having N,N-bidentate ligands have attracted interest, being the focus of many research, both because of their outstanding luminescent properties and because their role on photocatalytic processes. The luminescent processes on these kinds of complexes depend strongly on the nature of the ligands coordinated to the ReI carbonyl center. Derivatization of the ReI carbonyl center to produce new compounds with diverse properties generally goes through halide (X) removal by using a silver salt. The reaction between $[(N,N)Re(CO)_3(X)]$ and a silver salt to afford insoluble (then easily removable) silver halide is clean, quantitative and widely general. Within the available structure, the position left by the halide X upon removal is occupied by solvent molecules. In this work we show the spectroscopic properties of the $[(phen)(H_2O)Re(CO)_3]^+$ cation and relate these to those corresponding to the parent complex $[(phen)Re(CO)_3Br]$. The absorption and emission properties of this new complex have been evaluated using steady state and time resolved techniques. Luminescence lifetimes and quantum yields of singlet oxygen generation are reported and discussed.

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Photoactivated nanoparticles kill pathogenic bacteria but proved to be harmless to eukaryotic cells

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When a metal nanoparticle interacts with light, having a wavelength longer than the dimensions of the particle itself, Surface Plasmon Resonance (SPR) takes place. In case of gold, SPR absorptions occur in the visible range; this allows us to use cheap LEDs (525nm) as radiation source. The nanomaterial employed here was synthesized according to the procedure published previously (JACS REF2014). It consists of a gold core, encapsulated in a silver shell and stabilized with a dipeptide, specifically aspartame (Asp). The gold core is designed for efficient heat delivery through established plasmonic mechanisms. The silver shell retains the antibacterial properties that are now well characterized in the case of AgNP. The surface protection with aspartame (Asp) leads to excellent aqueous stabilization with long shelf life. Further, aspartame is non-toxic, remarkably inexpensive and easy to replace by another molecule of interest. Previous results showed that bactericidal activity was achieved after only 6h of low energy irradiation in samples treated with Asp@Ag@AuNPs. This could be attributed to the synergism between the silver shell and the plasmon excitation of gold core. In this work, ROS production is detected by Fluorescence Microscopy in *Staphylococcus aureus* ATCC 29213 and an extended-spectrum beta-lactamases-producing *Escherichia coli* treated with Asp@Ag@AuNPs and irradiated at 525 nm; while eukaryotic toxicity was evaluated with the MTT assay in fibroblast Balb/3T3 clone A31 (ATCC CCL-163) culture also under irradiation. Maximum ROS production was detected in *S. aureus* and *E. coli* after 2 and 3 hours of irradiation correspondingly, suggesting that oxidative stress would be the major cause of bacteria death. Cell survival percent was up to 98% even after 18 hours of irradiation using the same LED panel and nanoparticles concentration. The photoactivated nanoparticles

have proven to be able to kill completely the bacteria population and still remain harmless for eukaryotic cells under the same conditions. Further investigation will include a co-culture experiment to confirm these results.

Photolability of third generation antihypertensive 1,4-dihydropyridine drug: lercanidipine

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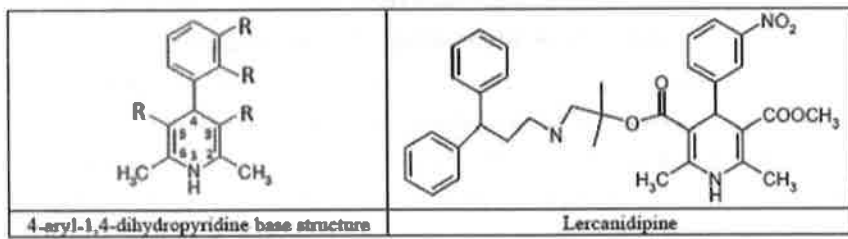
Compounds like 4-aryl-1,4-dihydropyridines are widely used drugs for the treatment of hypertension. There is a variety of drugs belonging to this family such as Nimodipine, Felodipine, among others. They all share the same basic structure, but they differ in the substituents attached to the 4-aryl moiety on the dihydropyridine ring. The photochemical and photophysical behavior of these drugs are strongly affected by the electronic nature of the substituents attached to the 1,4-dihydropyridine ring; the presence of electro donor substituents in the 4-aryl moiety decreases the photolability of these kinds of compounds [1]. These drugs have been linked to the induction of photoallergic and phototoxic effects in patients under prolonged treatments with them [2]. Some studies have reported that the incorporation of 1,4-dihydropyridines into supramolecular systems such as liposomes or vesicles, enhances the photo stability of these compounds [3] having in mind that these drugs are highly lipophilic. The kinetic results obtained for the third generation antihypertensive drug Lercanidipine are similar to those obtained for its homologue Nimodipine, which makes sense due to they only differ in the substituent attached to the position 3 of the dihydropyridine ring.

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Acknowledgements

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Photochemical properties of 6h-dibenzo[b,h]xanthene derivatives

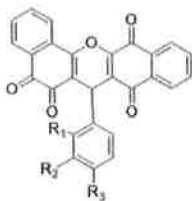
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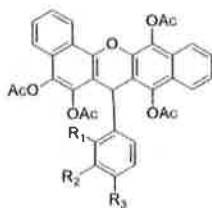
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Xanthene and its derivatives occupy an important position among dyes. In particular, benzoxanthenes have shown therapeutic and biological properties such as anti-bacterial, anti-viral and anti-cancer. Another application of this class is the use as photosensitizer. In the cell, for example, the activated photosensitizer can react by electron or hydrogen transfer, or through energy transfer to oxygen forming singlet oxygen. Both pathways can lead to tissue damage and cellular death. Given their importance, we have investigated the photochemical properties of 7phenyldibenzo[b,h]xanthene-5,6,8,13-tetraones (1a-d) and 7-phenyldibenzo[b,h]xanthene-5,6,8,13-tetrolacetates (2a-d). The absorption spectra for all compounds revealed solvatochromic blueshifts on changing the solvent from chlorobenzene to acetonitrile. Additionally, fluorescence experiments revealed emission maxima for 2a-d centered between 350 and 360nm. The quantum yield of fluorescence and the lifetime (Φ_f ; τ_f) were determined: 2a (0.23; 6.8ns), 2b (0.30; 6.6ns), 2c (0.16; 7.0ns), and 2d (0.25; 6.7ns). The laser flash photolysis of 1a, 1b, and 1c, in acetonitrile, resulted in the formation of the respective triplet excited states. These triplet states were quenched by phenol, indole and N-acetyl L-tryptophan methyl ester. In all cases a new transient was formed, which was assigned to the corresponding radical pair resulting from an initial electron transfer followed by a fast proton transfer. The quantum efficiency of singlet oxygen formation (Φ_Δ) was determined by employing time-resolved near-IR emission studies upon laser excitation: 1a (0.50), 1b (0.16) and 1c (0.24). In conclusion, it was shown that 1a-c can react via electron and hydrogen transfer as well as generate singlet oxygen and can act as photosensitizers with biological substrates. In addition, compounds 2a-d photoluminescent and could be useful as fluorescent probes.



- 1a** R₁=R₂=R₃=H
1b R₁=Cl, R₂=R₃=H
1c R₁=R₂=H, R₃=Cl
1d R₁=R₂=H, R₃=CH₃



- 2a** R₁=R₂=R₃=H
2b R₁=R₃=H, R₂=Cl
2c R₁=R₂=H, R₃=Cl
2d R₁=R₃=H, R₂=NO₂

Determination of excited singlet-state dipole moment of biopolymeric photoinitiator based on thioxanthone/chitosan using solvatochromic method

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The aim of this work was to study the absorption and fluorescence characteristics of new biopolymeric photoinitiator derivative of thioxanthone and chitosan in different solvents. The absorption and fluorescence spectra of 10-oxo-10H-dibenzene thiopiran-1-2-dicarboximide/chitosan (TXICH) in various solvents were obtained. Dipole moments in excited states were calculated using solvatochromic data. The ground state dipole moment (μ_G) was calculated by Density functional theory (DFT) method. Singlet excited dipole moment (μ_E) was estimated from three different methods proposed by Lipert-Mataga; Bakhshiev/Kawiski-Chamma-Viallet and Reichardt. The TXICH showed an intense absorption band in the range of 330-410 nm in all the solvents. This band can be attributed the $n-\pi^*$ e $\pi-\pi^*$ transitions. In aprotic solvents, stabilization of $\pi-\pi^*$ state and a blue shift of $n-\pi^*$ state occur. In the case of polar solvents (especially water), it was observed a large Stokes shift in the fluorescence emission spectra of TXICH. For hydroxylic solvents, these results suggest that in the S_0 and S_1 state, the compound act as proton acceptor and proton donor, respectively. Varying the solvent polarity, the shift emission peaks were more affected than absorption peaks, this behavior indicate that $\mu_E > \mu_G$. The μ_G value obtained by DFT was 2.3 Debye. The μ_E values estimated by Lipert-Mataga; Bakhshiev/Kawiski-Chamma-Viallet and Reichardt equations were 9.8, 9.5, and 8.3 Debye, respectively. The singlet excited dipole moment values obtained to biopolymer initiator TXICH were higher than the ground state, which is a indicative that the photoinitiator can be more polar in the excited state than in ground state.

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Synthesis and characterization of silver nanoparticles/clay nanocomposites via photochemical method

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In the last few years, the study about preparation and characterization of metallic nanoparticles is subject of great attention due their unique physical and chemical properties in nanoscale which lead to many potential applications. Among of metal nanoparticles, silver nanoparticles have been intensively studied due their different application areas such electronics, optical, catalysis and antimicrobial activity. Recently, some studies describe the preparation of silver nanoparticles using clays dispersed in solvent[1,2,3]. In this study silver nanoparticles (AgNPs) and AgNPs/clay nanocomposites were prepared by photochemical method from an aqueous solution of Irgacure-2959 and silver nitrate (AgNO₃). As stabilizer was utilized the sodium citrate (AgNPs/Citrate), sodium citrate and clay (AgNPs/Citrate/Clay) and pure clay (AgNPs/Clay). The clays utilized with support were the natural montmorillonite (SWy-1) and the synthetic clays (SYn-1 and Laponite). The formation of silver nanoparticles was recorded as a function of the UV irradiation time with a UV-visible spectrophotometer and the characterization was performed by Transmission Electronic

Microscopy (TEM) and Dynamic Light Scattering (DLS) techniques. The intensity of the absorption peak at about 391~405 nm in Uv-vis spectra of Ag colloidal increased with the irradiation time, indicating the silver nanoparticles formation. Transmission electronic microscopy images revealed that all AgNPs formed showed spherical morphology. The stabilizer utilized influenced on nanoparticles size. Also, the clay properties affected the size and stability of AgNPs. The AgNPs stabilized with only the Laponite clay presented a smaller diameter (<10 nm) than the AgNPs synthesized with SWy-1 and SYn-1 clays, because the exfoliated platelets of Laponite clay stabilizes the AgNPs more efficient than layered clay without exfoliation.

The stability of AgNPs is attributed to the high-aspect-ratio surface of the exfoliated platelets of Laponite clay. The AgNPs stabilized with Citrate/Clay presented a smaller diameter than AgNPs/Clay samples. In this case, the AgNPs stabilization could be assigned to the presence

of adsorbed citrate ions in the nanoparticles surface, originating electrostatic repulsion between the silver nanoparticles and avoiding the aggregation.

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Spectroscopic study of 1,1'-diethyl-2,4'-cyanine adsorbed on solid clays

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The dyes may be incorporated in a clay mineral matrix to cause an increased stability against photodegradation, chemical degradation, and thermal decomposition. Therefore, control of the properties of the dyes by using a mold suitable clay is a challenge for the development of a hybrid material dye/clay^{1,2}. The photophysical behavior of 1,1'-diethyl-2,4'-cyanine (IC) dye adsorbed onto solid clays was studied. The UV-Vis absorption spectra of IC (0.01 to 0.1%) incorporated in SWy-1 and Laponite RD clays present bands at 518 and 556 nm, indicating monomers of IC. It can be seen that increasing IC concentration, there is a hypsochromic shift of the bands together with a decrease in fluorescence intensity. This indicates the formation of H aggregates of the IC, since H aggregates not exhibit fluorescence. In the case of SAz-1 and SYn-1 clays, in lower concentration of IC, the appearance of a new band at 573 nm in the UV-vis spectra occurs, indicating the formation of J aggregates. For higher concentrations of IC (1% to 5%), the band at 482 nm increases and the band at 573 nm disappears. This indicates that H aggregates predominate. Thus, it is seen that the charge density of the clay affects the IC aggregation. SAz-1 clay has higher charge density than SWy-1, favoring the formation of J aggregates of IC. The basal spacing of pure Laponite RD and SYn-1 remain the same that for Laponite RD and SYn-1 containing 5% of IC. The adsorption of the dye predominantly occurs on the external surface of the Laponite RD and SYn-1 clays. XRD measurements confirm the penetration of the IC into interlayer regions of the SWy-1 and SAz-1 clays. When the IC is in the interlamellar regions of clay, its internal movements are restricted, reducing the rate of internal conversion. The adsorption of the dye occurs on the external surface and inside of SWy-1 layers. Acknowledgements: The authors would like to thank FAPESP, CAPES, CNPq and Contribution from the USP Research Consortium for Photochemical Technology (PhotoTech).

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Reduction of candida tropicalis biofilms by the photodynamic action of rubiadin, a natural anthraquinone.

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Enriched-anthraquinones (AQs) extracts of *Heterophyllaea pustulata* (Rubiaceae), have shown in vitro antifungal effect against *Candida* biofilms. Purified AQs from bioactive extracts exhibit photosensitizing activity. Antifungal activity of Rubiadin (RUB), a majority AQs from these extracts, was evaluated on *Candida tropicalis* biofilms, analyzing if this effect could be increased by irradiation and quantifying the reactive oxygen species (ROS) and reactive nitrogen intermediate. RUB, isolated from benzenic extract, was identified by their RMN data. Biofilm quantification was performed by the O'Toole & Kolter method on *C. tropicalis* NCPF 3111 and *C. tropicalis* clinical. RUB was tested at four concentrations in triplicate, under darkness and irradiation. The supernatant was used to measure the superoxide anion ($O_2^{\cdot-}$) production by the Nitro-Blue Tetrazolium (NBT) reaction, and nitric oxide (NO) generation by Griess reagent. The total system antioxidant capability was determined by FRAP assay and the activation of SOD by NBT assay. Amphotericin B (AMP B) was used as control. RUB decreased the biofilms formation of both strains only under irradiation, being the reduction percentage (%R) on the clinical strain ($82.1 \pm 3.0\%$) greater than the observed over reference strain ($61.2 \pm 4.8\%$) at the same concentration ($1.98 \mu\text{g/mL}$); even RUB achieved a higher %R than AMP B ($61.2 \pm 4.8\%$ at CIM). The observed decrease in both biofilms was correlated with an increase in the production of $O_2^{\cdot-}$ and NO. Moreover, no activation of SOD was observed, but there was an increase in total antioxidant system. In conclusion, in vitro antifungal activity of RUB against biofilms of *C. tropicalis* is mediated by a photodynamic mechanism: $O_2^{\cdot-}$ production (Type I), together with the activation of the total antioxidant system that not allowed the complete biofilm elimination. Therefore, it would be promising evaluate the effect of consecutive periods of irradiation to achieve the biofilms eradication.

Estudio de los estados excitados del colorante eosina-y en presencia de dendrímeros en solución acuosa

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La búsqueda de sistemas eficientes para la iniciación de polimerizaciones que no afecten el medio ambiente es relevante en estos tiempos. En este sentido, el empleo de radiación visible, iniciadores de baja toxicidad y agua como solvente es de gran interés. Los dendrímeros son macromoléculas altamente ramificadas y simétricas que dependiendo de su tamaño (generación), pueden formar estructuras globulares en solución [1]. Esto permite la formación de cavidades internas capaces de alojar moléculas más pequeñas en su interior. Los dendrímeros PAMAM son biocompatibles y poseen grupos amino primarios en la superficie y terciarios hacia el centro de la macromolécula, que podrían actuar como dadores de electrones ante un colorante en estado triplete excitado. Los radicales amino así formados serían capaces de iniciar un proceso de polimerización con distintos monómeros [2]. Debido a que las aminas terciarias son dadoras de electrones más eficaces que las primarias, el tamaño del dendrímero y el grado de asociación con el colorante podrían influir en la eficiencia de generación de radicales iniciadores de la polimerización vinílica. Con vistas a esta aplicación, es necesario caracterizar previamente el comportamiento fotofísico y fotoquímico del colorante en función de la generación del dendrímero. En este trabajo se presenta un estudio de los estados excitados de la Eosina-Y en solución acuosa alcalina, frente a dendrímeros PAMAM de distintos tamaños. Los espectros de fluorescencia presentaron corrimiento batocrómico y disminución progresiva en la intensidad con el incremento en la generación del dendrímero. Las constantes de asociación (K_{bind}) obtenidas mostraron una fuerte dependencia con el tamaño de la macromolécula. Los gráficos de Stern-Volmer mostraron desviaciones de la linealidad y a partir de las determinaciones resueltas en el tiempo se obtuvieron dos tiempos de vida para el estado singlete. Mediante láser flash fotólisis (LFF) se pudieron registrar los espectros de absorción transitorios correspondientes al estado triplete y a la especie semi-reducida del colorante en presencia de PAMAM. Las respectivas constantes de desactivación del triplete (k_q) para el proceso de transferencia electrónica fueron cercanas al valor difusional y crecientes con la generación del dendrímero. Se obtuvieron los rendimientos cuánticos de formación de radicales para dendrímeros de distintos tamaños. Los estudios del singlete sugieren la presencia de dos especies emisivas del

colorante debido a su asociación parcial con el dendrímero. Los resultados de LFF mostraron un proceso de transferencia electrónica altamente favorable desde los dendrímeros hacia el colorante en estado triplete excitado. Se concluye que el sistema Eosina-Y/dendrímero sería un promisorio iniciador de polimerizaciones radicalarias, ecológico y de alto rendimiento.

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Photophysical properties of a novel rhenium (I) tricarbonyl complex with norharmine as ligand.

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β -carbolines are a group of naturally occurring alkaloids derived from 9H-pyrido[3,4-b]indole or norharmine (nHo). These alkaloids are widespread in biological systems, having an active role in different photosensitizing processes. Tricarbonyl rhenium complexes with polypyridyl and bioactive molecules as ligands have an excellent thermal and photochemical stability being, thus, appealing candidates for diverse applications such as photodynamic therapy. We show herein preliminary results about emission spectroscopy and flash photolysis studies of a novel $\text{Re}(\text{CO})_3(\text{bpy})(\text{nHo})^+$ in different solvents. UV-Vis absorption spectra show intense bands in the UV region of the spectra. These spectral features are almost identical with those found in the electronic spectrum of the free nHo ligand and are therefore assigned to $1L$ excitations in the nHo ligand. The absorption band observed in the visible region exhibit typically intense and solvatochromic MLCT transitions from the metal d to the lowest lying ligand p^* orbital. Emission spectrum of the complex, recorded in methanol, shows an emitting band at ~ 450 nm due to the deactivation of the lower nHo ligand-localized state, as it was described for free nHo. Emission from MLCT $\text{Re} \rightarrow \text{bpy}$ excited state have been observed in 530-560 nm range. Moreover, the observed luminescence shows a strong dependence on the oxygen concentration. Both emission quantum yield and lifetime values, obtained in all solvents tested, are compared with those reported for free nHo. The absorption patterns of the transient were registered by laser flash photolysis experiments, $\lambda_{\text{exc}} = 351$ nm. The absorption spectra in MeOH of the transient in N_2 atm. showed a maximum at 370 nm and a lifetime of ~ 125 ns. The redox activity of the excited state was measured by reductive quenching using TEA. Additionally, the efficiency of singlet oxygen production was determined in acetonitrile.

Spectroscopic analysis of chlorine aluminum phthalocyanine in binary water/ethanol systems

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The aim of this study was to evaluate the behavior of chlorine aluminum phthalocyanine in binary water/ethanol mixture by electronic absorption spectroscopy and static and dynamic fluorescence emission. The absorption and fluorescence spectra and Resonance Light Scattering of AlClPc in mixtures of water / ethanol at various concentrations were studied. The absorption spectra have presented drastic changes around 60% of water. Below 60% water, the AlClPc showed to be predominantly in the monomeric form. The dimerization constant values for the mixtures with 30 and 50% water were 7270.4 and $5982.8 \text{ L mol}^{-1}$, respectively, indicating that the formation of aggregates under these conditions is not favored. The value of dimerization constant at 60% water was estimated at $1937.0 \text{ L mol}^{-1}$ indicating the presence of dimer at this condition. The appearance of new bands at 387 nm and 802 nm from 60% of water and its bathochromic shift relative to the monomer bands position suggested that the J aggregates type are formed. Above 60% water, aggregation process was responsible for the complex balance between several large aggregates (as trimers, tetramers or oligomers) formed in the medium. Large aggregates showed non-fluorescent properties compromise photodynamic activity. These results have direct relevance in the better understanding on the behavior of these molecules in vivo, when incorporated in a Drug Delivery Systems as a DNA thin film. The DNA thin films have great potential for being a new generation of Drug Delivery Systems with high biocompatibility and stability what is the goal of these work.

Fluorescence lifetime of chlorine aluminum phthalocyanine into unillamellar mixed lipid vesicles

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The mixed lipid vesicles at containing AICIPc were prepared by ethanolic injection method. The lipid ratios used were 0.69:0.00:0.31 (DDS_I), 0.552:0.138:0.31 (DDS_{II}), 0.345:0.345:0.31 (DDS_{III}) and 0.207: 0.483: 0.31 (DDS_{VI}) mol% to 1,2-Distearoyl-sn-glycero-3-phosphocholine:1,2-Dioleoyl-sn-glycero-3-phosphocholine:cholesterol, respectively. Ethanolic solutions were prepared by weighing of lipids following by dissolution in anhydrous ethanol with the addition of stock solutions of AICIPc in ethanol, to rich a final concentration of 3.0×10^{-6} mol l⁻¹. The final lipid concentrations were 9.0×10^{-4} mol L⁻¹ for all DDS. The vesicle formations of controlled size were confirmed by Dynamic Light Scattering. Time-Resolved Confocal Fluorescence Microscope MT200 (PicoQuant, Inc.) with excitation wavelength of 640 nm by a picosecond diode lasers was used in fluorescence lifetime measurements. The experimental curve fitting were made by SymPhoTime software. The AICIPc showed a single lifetime of 6.25 ns in ethanol related to its monomeric form while two lifetimes were observed for AICIPc in all DDS. The lifetimes were: 5.38 (92.72%) and 1.62 (7.28%), 4.95 (90.46%) and 1.29 (9.53%), 5.53 (95.22%) and 1.97 (4.78%) and 5.16 (87.15) and 1.96 (12.85%) for AICIPc into DDS_I, DDS_{II}, DDS_{III} and DDS_{VI}, respectively. The biggest fluorescence lifetime seems to be related to AICIPc incorporated in its monomeric form while the shorter is due to dimmers aggregates of AICIPc. The decrease in longer fluorescence lifetime of AICIPc in DDS compared to homogeneous medium suggests shallow location, once this is the accessible site to water molecules that can act as quencher of fluorescence lifetime. Thus, AICIPc presented a single interfacial location in mixed lipid vesicles regardless of their degree of unsaturation.

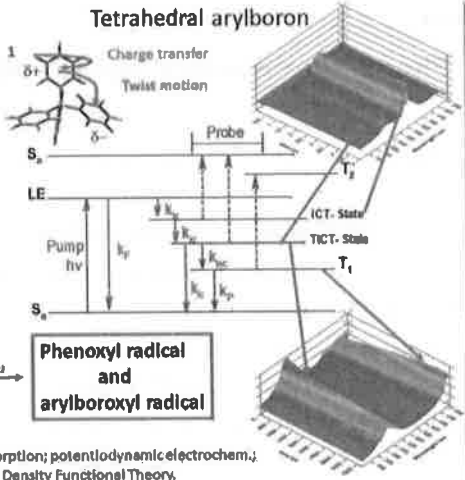
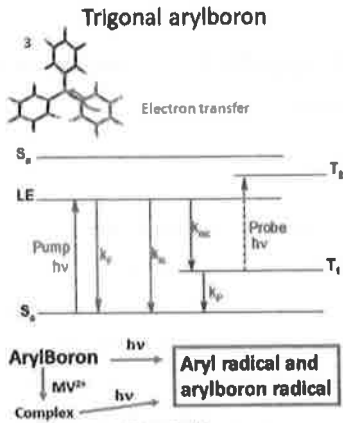
Excited state reactivity of trigonal and tetrahedral arylboron compounds as revealed by dft, steady-state spectroscopic and ultrafast transient absorption studies

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Tetrahedral arylborates was shown by ultrafast transient absorption spectroscopy to form a pi-orbital coupling between two adjacent aryl groups as revealed by the direct observation of the twist intramolecular charge transfer band (TICT) centered at 680 nm with a lifetime of 6.7 ns in hexanol at 298 K. The formation of the excited TICT-state was not observed for trigonal arylboron compounds as supported by ab initio density functional theory (DFT) calculations that shows lack of orbital symmetry in the ground and excited-state. By different pathways, the TICT and S₁ excited states from respective tetrahedral and trigonal boron compounds pass nonradiatively to triplet-state. Both of those triplet-state of tetrahedral and trigonal compounds decays to form aryl and diphenylboron radicals in the absence of oxygen. EPR signal of aryl-DMPO and aryl-PBN adducts were identified by similar coupling constants from literature. boron-adducts were identified by coupling constants of ¹⁰B and ¹¹B on adduct contribution. In the presence of oxygen, aryl-oxyl and boron-oxyl radicals were identified by specific coupling constants of respective adducts with DMPO molecule. Different from trigonal arylboron, tetrahedral arylborates were shown to form a charge transfer complex with methyl (MV₂⁺...2B(aryl)₄) displaying an absorption band at 405 nm arising from the interaction of pi-orbitals of the aryl-groups in the boron compound with the N-positively charged atom in methylviologen as supported by FT-IR. Light excitation of the (MV₂⁺...2B(aryl)₄) complex at 355 nm shows the formation of a triplet radical pair with T-T absorption band at 450 nm (time decay = 2 us) which decays to MV^{••} (at 605 nm and time decay > 10 ms) and radical photoproducts from B(Ph)₄. Major product of radical recombination were characterized by high resolution mass spectroscopy.



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EPR; LFP; SPC; Ultrafast transient absorption; potentiodynamic electrochem.; High resolution mass spectroscopy and Density Functional Theory.

Photoinduced autophagic cell death: an efficient mechanism to kill tumor cells

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Photodynamic Therapy (PDT) uses photosensitizer (PS) and light in a suitable wavelength, generating photoinduced reactions which promotes photooxidation of biomolecules.[1] The amphiphilic character of the PS is usually associated to a larger partition on biological membranes and consequently high cellular photodynamic activity.[2] In addition, it is known that intracellular localization of the PS in specific cell organelles may have strong influence in cell death mechanisms.[3] In general, drugs that accumulate in the cytoplasmic membrane tend to trigger cell death by necrosis, whereas those targeting intracellular organelles such as mitochondria, endoplasmic reticulum and lysosomes tend to favor programmed cell death mechanisms (apoptosis and/or autophagy) depending on the photosensitizer and light dose.[4] Autophagy is an important cellular program that promotes either cell survival or cell death. The survival role occurs by recycling cell components during starvation or removing stressed organelles; while cell death role also occurs by recycling cell components but here in presence of extensive damages in organelles (mitochondria and/or lysosomes) in a way that autophagy fail in recycle cell components, resulting in a programmed cell death pathway, known as autophagic cell death.[5] Because autophagy is a lysosome-dependent degradative pathway,[6] lysosomes organelles have important role in autophagic flux, since these organelles provide suitable environment (acid organelles and specific enzymes in the digestion process) to proceed this cellular program.[7] Thus, when these organelles are damaged it may compromising survival/death balance causing autophagic cell death.[5] Recently, Berg and colleagues presented a new strategy to allow drug or biomolecules delivery inside eukaryotic cells using photosensitization effects at a sub-dose level, which they named photochemical internalization (PCI).[8] This concept is based on the use of photosensitizers (PSs), which localize preferentially in endocytic/lysosomes vesicles, photodamaging these organelles membrane and providing for the classical therapeutic agents escape mechanism of endo/lysosomes.[9] In general, PCI technology uses amphiphilic anionic photosensitizers such as TPPS2a, AIPcS2a and TPCS2a., because these molecules are taken-in by endocytosis and

end up accumulating quite specifically in the membranes of endosomes/lysosomes vesicles.[10] In order to understand the consequences of a simple modification in the charge of PSs on the cellular localization and photodynamic efficiency, we have investigated the relationship between structure/charge and photoactivity of two photosensitizers with similar photophysical properties and structures, but opposite charges. The positive charged porphyrin (CisDiMPyP) presented higher level of interaction and uptake in three different membrane systems used (liposomes, erythrocytes and HeLa cells) than the negative charged porphyrin (TPPS2a). The photodynamic efficiency in erythrocytes and giant unilamellar vesicles (GUVs) was also higher to CisDiMPyP than TPPS2a, demonstrating that the photoactivity is directly associated to the interaction of porphyrin in membranes. Surprisingly, the phototoxicity experiments in HeLa cells showed higher efficiency to TPPS2a (IC50 3.5 times less) instead of CisDiMPyP, even TPPS2a present lower uptake in HeLa cells. In order to understand the reason of this, we also evaluated the mechanism of cell death for both porphyrins. Acridine orange (AO) and propidium iodide (PI) double staining experiments showed a large fraction of the cells presenting red PI fluorescence in HeLa cells treated with 100nM CisDiMPyP 3 hours after photoactivation, indicating necrosis as mechanism of cell death for this porphyrin. While HeLa cells treated with 30nM TPPS2a 3 hours after photoactivation showed almost absence of AO stained acidic vacuoles environments compared with control cells, suggesting the reduction in the number of viable lysosomes, and consequently damage on these acid organelles at this time point. Interestingly, 48 hours after photosensitization, TPPS2a-treated cells showed a lot more acid vacuoles stained with AO compared to the control, indicating the possible accumulation of autophagic vacuoles. It means that even both photosensitizers present similar photophysical properties and structures (both are amphiphilic), but the opposite charges of porphyrins induce affinity to different organelles resulting in distinct mechanisms of cell death. Therefore, we not only confirmed the need to use negatively charged amphiphilic PS for PCI technology (because the lysosome damage) but we also detected the induction of autophagy as mechanism of cell death caused by the photosensitizer TPPS2a, which is one of the commonly used in PCI. It suggests that Photochemical Internalization (PCI) may be a "fortified PDT" version not only because it function as system for site-specific drug delivery, but also because the intracellular target is selective providing autophagic cell death.

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Strategies for sequence-specific dna fluorescent labelling studied by super-resolution optical microscopy

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Sequence-specific DNA fluorescent labelling is a crucial issue to the success of DNA optical mapping and in vivo imaging. This labelling reaction is normally performed by a two-step methodology. At first, the methyltransferase enzyme targets the sequence 5'-TCGA-3' for modification with a functional group transferred from an analogue of the S-adenosyl-L-methionine (AdoMet) cofactor. In the second step, a fluorophore is coupled. In this contribution, we propose the investigation of an optimal methodology for sequence-specific DNA fluorescent labelling monitoring by superresolution optical microscopy and checking the structures by AFM images. pUC19 plasmids were modified with alkyne, azide or amine functional groups using M.TaqI enzyme. Subsequently, the fluorophore coupling was performed by copper-catalysed azide-alkyne cycloaddition (CuAAC), strainpromoted azide-alkyne cycloaddition (SPAAC), or amine-to-NHS-ester coupling. We also developed a single-step methodology that directly couples a fluorophore from AdoMet to DNA. Our single-molecule protocol counts the number of fluorophores associated with individual plasmids. The superresolution microscopy assays showed that 60% of plasmids labelled using the two-step CuAAC chemistry carry at least one fluorophore, with a total of four labelling sites available on each plasmid. However, the AFM images showed that the most part of the plasmids is in the open circular form and not in their native structure, which is supercoiled. This problem was not detected for SPAAC and amine-to-NHS ester coupling, which have also shown a low efficiency of the fluorophore-coupling step. However, for the direct one-step enzymatic transfer of fluorophores to the DNA was able to attach at least one fluorophore to over 80% of the plasmids. Besides, AFM images confirmed that the native conformation was retained. The plasmids labelled by the direct reaction were successfully applied to transfection into mammalian cells.

Isomerization of vit. D3 through energy transfer as a protective mechanism against flavin sensitized photooxidation

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Vitamins have varying reactivity depending on their biological functions. For some vitamins, the reactivity is modulated in pro-vitamins with better stability, and the vitamin function depends on an activation step. The lipophilic vitamin D provides such examples as 7-dehydrocholesterol is found as a pro-vitamin D in food of animal origin and ergosterol is found as pro-vitamin D in food from the plant kingdom. The activation step involves for both pro-vitamins a photochemical reaction to form cholecalciferol, vit.D3, or ergocalciferol, vit.D2, respectively, as occurring in human skin upon exposure to UV-B sunlight. Among the water-soluble vitamins, vitamin B2 is also photoactive since riboflavin, the form of vitamin B2 normally in foods, and the biological forms of vitamin B2, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD), are potent photosensitizer inducing oxidative damage in food and skin including degradation of the isoalloxazine ring common for these flavins. Cholecalciferol, vit. D3, was found to isomerize to 5,6-trans-vitamin-D3 with a quantum yield of 0.15 ± 0.01 in air-saturated tert-butanol/water 7:3 (v/v) at 25 °C, increasing to 0.32 ± 0.02 in absence of oxygen, through quenching of $^3\text{FMN}^*$ rather than to become oxidized. The quenching was found by laser-flash photolysis to have a rate constant of $1.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ in tert-butanol:water 7:3 v/v at 25 °C assigned to energy transfer from $^3\text{FMN}^*$ to form a reactive vit.D3 diradical. Vit.D3 forms a 1:1 precomplex with FMN by hydrophobic stacking with $\Delta H^\circ = -36 \pm 7 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\circ = -4 \pm 3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ as shown by single photon counting fluorescence spectroscopy and steady state fluorescence spectroscopy. Both ground state precomplex formation and excited state energy transfer seem important for vit.D3 protection against flavin sensitized photooxidation of nutrients in food.

Chemical physics dynamics of proton transfer at the ground and excited states of ortho-(2imidazolyl)naphthols

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Photoacids are molecules that become strong acids at the excited electronic state[1]. Typically, these molecules 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]. This project aim for the study of the following naftol series: 1-(1H-imidazol-2-il)naftalen-2-ol (1NI2OH), 2-(1H-imidazol-2-il)naftalen-1-ol (2NI1OH), 3-(1H-imidazol-2il)naftalen-2-ol (3NI2OH), in order to understand the dynamics mechanisms of the photo induced proton transfer reactions (ESIPT and ESPT), connecting with the solvent role. We obtained absorption and emission spectra of the three compounds in different solvents. By increasing polarity, and the solvation of the phenol moiety, a blue shift is observed on the absorption spectra. The effect is more intense to 1NI2OH, except to the spectra in water because of the strong intramolecular hydrogen bond. The emission spectra do not have a clear tendency, since the imidazole moiety is not on the same plane of the naphthalene ring. But the other compounds exhibit a blue shift with the solvent polarity increase, which means that there is a preference for the intramolecular interaction in the excited state (in favor of the ESIPT). Regarding the 3NI2OH, the emission spectra shows the two bands of the tautomeric forms that appear as a consequence of the photo induced reaction. We also performed time resolved experiments to determine pK_a^* in strong acid conditions. In addition to the determination of the fluorescence lifetimes in different solvents, proving the steady-state spectral tendencies. The comparative study of the fluorescence lifetimes also offered the parameters to appoint an ESIPT reactivity order through the association of emissive decays and steady state emission spectra (Decay Associated Spectra – DAS)[3]. The DAS's showed that the 3NI2OH is more reactive than the others and the 2NI1OH is the less reactive. Considering the results, we assume that is more likely that the 2NI1OH transfers the proton to the solvent.

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Nanomaterial based on silicon phthalocyanine supported on zeolite surface: potential environmental application using sunlight

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Nanosystems based on photosensitizer dyes supported on silica have been widely investigated for the generation of singlet oxygen with numerous applications from medical to environmental chemistry. Silicon phthalocyanine (SiPC), when excited with the proper wavelength, has great efficacy in generating singlet oxygen, which is cytotoxic. However, SiPC has a tendency to form aggregates, and hence, the formation of this reactive species of molecular oxygen turns to be inefficient. Nanozeolite L is a well-known material to covalently support phthalocyanine (SiPC) on its surface to prevent this aggregation process. In this study, a nanomaterial (nZeol-SiPC) was prepared by covering the surface of zeolite L (crystal size: 30-60 nm) with SiPC molecules. Additionally, (3-aminopropyl)-triethoxysilane (APTES) was linked to the surface of the zeolite L in order to promote a positive charge distribution on the bulk material, when it is dispersed in water. By this procedure, the positively charged zeolites can electrostatically interact with negatively-charged cell membranes. This nZeol-SiPC material was characterized by thermogravimetric analysis and spectroscopic methods. Tests have been carried out using nZeol-SiPC functionalized with APTES in phosphate-buffered saline solution (pH 7.4) under the exposure of sunlight ($\sim 1000 \text{ W/m}^2$) in different time intervals to evaluate the efficiency of this nanomaterial in the photoinactivation of mouse fibroblast cells (BALB/c 3T3 clone A31). A very high efficiency of this nanomaterial could be verified by cell viability tests, in which 90 % of the BALB/c cells died within 30 minutes. These results suggest the possibility to use this nanomaterial in the photoinactivation of pathogenic species in contaminated water using sunlight. Currently, our group is performing tests using *E. coli* bacteria.

Interaction of phenothiazinium dyes methylene blue and do15 with dopc membranes

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Photodynamic therapy (PDT) is a clinical modality that exploits the combination of light, molecular oxygen and a photosensitizer (PS) to eliminate tumor cells or pathogens. The mechanism behind PDT relies on the excitation of the PS to a singlet excited state, which in turn can generate a triplet excited state. This longer lived excited state can transfer electrons or energy to molecules nearby, forming reactive species that can damage biomolecules and promote cell death. Singlet oxygen is often considered the leading reactive species for PDT. Amongst the many types of PS that can be used in PDT, phenothiazinium dyes are a promising alternative to the classically employed photosensitizing agents. For instance, methylene blue (MB), the most well-known representative of this class of molecules, is an efficient singlet oxygen generator, absorbs light in the so called therapeutic window and is cheaper than many other PS. The main goal of this work is to clarify the mechanisms operating in PDT, specifically in the case of interactions between PS and membranes. For this purpose, we compared the interaction of MB and the more hydrophobic phenothiazinium dye DO15 with 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) membranes, trying to identify key factors leading to photodynamic efficiency. Both molecules have similar singlet oxygen quantum yields (ca. 0.5, in ethanol) and molar absorption coefficient of $\sim 105 \text{ M}^{-1} \text{ cm}^{-1}$, as determined previously. To start with, the absorption spectra of MB and DO15 in water were compared to the spectra of these same dyes in DOPC liposomes aqueous suspensions. We observed the presence of MB aggregates in both conditions, and the absorption profile of the dye varied very slightly between both conditions. The formation of aggregates is often regarded as a disadvantage to photodynamic efficiency, since it reduces singlet oxygen generation. On the other hand, DO15 disaggregated upon addition of liposomes, as seen by an increase of the monomer's absorption intensity and a small increase in the ratio between the monomer's and the aggregate's absorption intensity. These results were in accordance with the partition ratio P

measured for both dyes in DOPC liposome suspensions. For DO15, $P = 1.8 \pm 0.1$, whereas for MB this value is 0.03 ± 0.04 , showing that the former binds to a greater extent to DOPC liposomes than the latter. Being DO15 a more hydrophobic dye, probably binding to the lipid bilayer decreases hydrophobic-effect driven aggregation. In addition, DOPC liposomes containing a fluorescent probe that can be used to detect membrane permeabilization were also irradiated in the presence of these PS. We observed that DO15 led to membrane permeabilization, whereas no effect was observed for MB. In order to broaden our observations, we also compared the effect of both dyes in giant unilamellar vesicles (GUVs) made of DOPC. In this case, phase contrast microscopy was used to assess membrane permeabilization. MB had almost no effects on the GUVs in the dark, while DO15 led to explosion of some vesicles and permeabilization of others. This suggests that the DO15 molecule per se has a greater effect on the structure of the lipid bilayer than MB, probably destabilizing it. When light was shed on the vesicles incubated with the dyes, we observed that both PS led to membrane permeabilization, which was faster for DO15. This light-dependent effect was much more evident than the permeabilization that occurred in the dark, showing that the activity of DO15 is significantly enhanced in the presence of light. Taking all these observations into account, we can hypothesize that the higher efficiency of DO15 to damage membranes both in the presence and in the absence of light can be explained mostly by its greater affinity to membranes. Once bound to the membrane, the photodynamic activity of DO15 is further increased, since the lipid bilayer lowers the extent of aggregation. This allows the generation of reactive species close to the lipids, leading to the reactions that ultimately cause membrane permeabilization.

Parietin, an anthraquinone derivative isolated from *teleoschistes flavicans*, as photosensitizer type I

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For several years, anthraquinone (AQs) derivatives have been thoroughly studied in relation to their photosensitizing properties in photodynamic reactions. Some of them have shown good antibacterial and antiviral effects by means of photosensitization, in where reactive oxygen species (ROS) are increased, such as superoxide anion (O_2^-) (Type I mechanism) and singlet molecular oxygen (1O_2) (Type II mechanism), and the subsequent oxidative damage is observed [1]. This time we report the type I photosensitizer properties of parietin (PTN), an AQ isolated from the lichen species: *Teleoschistes flavicans* (SW) Norm. (Telochistaceae) [2]. The production of O_2^- was detected and quantified with an indirect photobiological method, which measures the reduction of Nitroblue Tetrazolium (NBT) to blue formazan by O_2^- generated inside human leukocytes, when an oxidizer (AQPTN) is present in the dark and under continuous UV-Vis radiation (380–480 nm, with a maximum at 420 nm - 0.65 mW/cm²). The absorbance of blue NBT formazan intracellular was measured with respect to basal production and was expressed in percentage. According to the results, PTN causes an increase in the production of O_2^- under irradiation compared to darkness condition at 5 and 10 mg / ml (Table 1). At 20 mg/mL and darkness, the percentage of production of O_2^- is less than those generated to 5 and 10 mg/mL and even under irradiation, this percentage was equal to the condition basal (0.0 ± 0.0). These latter results could be due to an excessive generation of ROS in dark condition and even more under irradiation at 20 mg/mL, causing a major oxidative damage in the leukocytes with the eventual cell death. In conclusion, it was shown that PTN is a good photosensitizer type I and this is directly dependent on the concentration used.

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Table 1: O₂⁻ generation in human leukocytes produced by PTN (5, 10 and 20 µg/mL). Assay of NBT reduction in dark condition and with UV-V radiation.

AQ	5 µg/mL		10 µg/mL		20 µg/mL	
	Dark	Irradiation	Dark	Irradiation	Dark	Irradiation
PTN	140.8 ± 15.1	198.6 ± 21.8	367.8 ± 28.4	963.6 ± 37.5	122.7 ± 18,0	0.0 ± 0.0

Chlorinated anthraquinones as type I photosensitizers

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Heterophyllaea lycioides (Rusby) Sandwith grows in the Andean region from Bolivia and Perú, and is one of the two species which forms *Heterophyllaea* genus. From aerial parts, we purified two new anthraquinones (AQs) derivatives for this family of compounds, both characterized by the presence of chlorine in their structures: 5-clorosoranjidiol y 7-clobisoranjidiol. Worth noting that is the first time that AQs containing chlorine are reported for a species of Rubiaceae. Previously, we demonstrated that AQs isolated from the other vegetal specie, *H. pustulata*, are photosensitizers by acting through type I and/or type II mechanisms. Continuing this research line, we propose to determine whether new chlorinated AQs are able to generate superoxide anion radical ($O_2^{\cdot-}$) under irradiation (type I mechanism). $O_2^{\cdot-}$ production was quantified by an indirect photobiological method, which measures the reduction of Nitroblue Tetrazolium (NBT) to Formazan Blue (FB) by action of the $O_2^{\cdot-}$ generated for human leukocytes (2×10^6 cells/ml), when an oxidizer (AQ) is present. This assay was performed under darkness vs. UV radiation (290–400 nm, UVR). Samples were tested at two different concentrations: 10 and 20 $\mu\text{g}/\text{mL}$ in Hank's balanced salt solution (HBSS) with DMSO (1%) as co-solvent. Cell controls and samples ($n=2$) were incubated at 37 °C for 30 min, under both experimental conditions. Absorbance of FB was measured at 575 nm. The increased of $O_2^{\cdot-}$ production respect to controls was expressed in percentage (Fig. 1). Results show that 5-clorosoranjidiol only produced stimulation of $O_2^{\cdot-}$ at 20 $\mu\text{g}/\text{mL}$, whereas the chlorinated dimer increased it at 10 $\mu\text{g}/\text{mL}$ and not at the highest concentration tested. This could be due to a high generation of this reactive species, promoted for this concentration; and thus the $O_2^{\cdot-}$ generated may be attacking several cellular components, leading to eventual cell death. In conclusion, we demonstrated that 5-clorosoranjidiol and 7-clorobisoranjidiol generate photosensitization in vitro by type I mechanism, which is directly dependent on the concentration used.

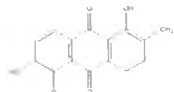
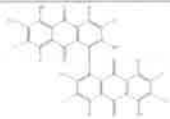
Concentrations tested	Conditions	 5-clorosoranjidiol	 7-clorobisoranjidiol
10 µg/mL	Darkness	38,2 ± 1,7 %	47,5 ± 1,8 %
	UVR	27,8 ± 5,9 %	75,9 ± 13,5 %
20 µg/mL	Darkness	19,67 ± 7,0 %	54,1 ± 6,6 %
	UVR	59,0 ± 5,3 %	45,9 ± 6,3 %

Fig. 1: Stimulation of oxidative metabolism in human leukocytes, under darkness and irradiation conditions.

Natural photosensitizers and the effect of visible light in skin and hair

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Protection of human skin against sun exposition is a complex issue and needs the understanding of ambivalent aspects of the interaction of light and tissues. One misconception that has persisted is that visible light is safe to the skin, even though several data suggest the opposite. Here we will present the main photosensitizers naturally present in human skin and hair that absorb in the visible part of the spectra, which are: flavins, melanins, lipoofuscin. We will describe their photophysical properties and the biological response they cause in different experimental systems. In the presence of these chromophores, visible light induces very similar effects as those observed for UVA radiation, triggering photosensitization reactions that damage membranes, proteins and DNA of epithelial cells. Changes in cellular homeostasis vary from cell death by necrosis, autophagy, apoptosis or induction of senescence, depending on the level of cellular damage. Irrefutable data indicate direct oxidation in nuclear DNA, which can have severe consequences in the genomic stability. Some of these chromophores are also present in hair and are responsible for the effects of visible light in the color and properties of hair. We aim to discuss the data obtained in different experimental systems to get to comprehensive view of the effect of visible light in human skin and hair.

Photopolymerization synthesis of hydrogels: release studies of non-steroidal antiinflammatory drugs.

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Synthesis and characterization of hydrogels employing a modified silsesquioxane with amino and methacrylate groups as co-initiator and crosslinking agent was carried out. The presence of these functional groups in the modified silsesquioxane provides a double role: the amino groups act as co-initiators, while the presence of several acrylate groups makes this compound a good crosslinking agent [1]. The synthetic dye safranin was used as sensitizer of the polymerization reaction in order to employ visible light [2]. Hydrogels were synthesized with a 10:90 weight ratio of acrylamide: 2-hydroxyethyl methacrylate. The synthesis was carried out using different proportions of the modified silsesquioxane, allowing modulating the properties of the materials as systems suitable for controlled drug release. Hydrogels prepared in this way were characterized using several techniques such as: SEM, FTIR and DSC. Their ability to swell as function of pH and temperature was also investigated. The results show that the percentage of modified silsesquioxane employed affects the swelling capacity of the hydrogels. Thus it is possible to modulate the properties of the materials from variation of crosslinking agent in the formulations. Additionally, incorporation assays of non-steroidal anti-inflammatory drugs aspirin and ibuprofen during the photopolymerization process were carried out. Reagents were successfully incorporated without changing the properties of synthesized hydrogels. Furthermore, the active drugs were not altered by the photopolymerization reaction. This technique facilitates the incorporation of higher amounts of drugs compared to other conventional methods of incorporation such as posterior absorption [3]. Release studies were followed by spectroscopic techniques. The experimental results were fitting by the empirical equation proposed by Peppas and col. [4]. It was found that the release of these drugs depends on the composition of the hydrogels and the pH of the medium in which the liberation takes place. In most cases a progressive release of over 80% was achieved. Cytotoxicity studies showed

that these materials do not exhibit hemolytic activity, which would make them suitable as new biocompatible systems for controlled drug release.

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Singlet oxygen generation enhanced by silver nanoparticles biological applications

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The cytotoxic effect of singlet oxygen is currently used in photodynamic therapy (PDT), where the controlled production of singlet oxygen leads to the eradication of undesired tissue [1]. The inefficient production of singlet oxygen can limit the use of PDT photosensitizers, so metal-enhanced singlet oxygen generation is a desired effect. Recently, using Riboflavin (Rf) as the sensitizer, the enhancement of singlet oxygen generation by pectin-coated silver nanoparticles (AgNPs) was demonstrated by indirect methods [2]. In this work, we investigate the effect of AgNPs on the singlet oxygen generation by Rf by time-resolved phosphorescence (TRP) of singlet oxygen at 1270 nm. The cell damage caused by the sensitizer with and without AgNPs, when the cells were exposed to light, was also evaluated. The AgNPs were prepared by a modification of the procedure reported in reference [3]. The method is based on the reduction of AgNO₃ with pectin in basic medium. The average diameter of the AgNPs (13±6 nm) was measured by atomic force microscopy. The UV-Vis spectroscopy showed that the maximum of the plasmon absorbance of the AgNPs is located at 410 nm. The TRP data confirm the metal enhanced production of singlet oxygen by Rf in the presence of AgNPs and show the singlet oxygen generation upon excitation of the AgNPs in the plasmon band (420nm). HeLa cells were incubated with the Rf with and without the AgNPs and irradiated at 420 nm. Irradiated cells treated with Rf and AgNPs showed necrosis 15 min earlier than those treated under similar conditions but without the particles. These results are in agreement with the TRP data.

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Experimental and theoretical study of effect of the zn coordination complex on the excited state and two-photon absorption spectra of salicylidene compounds

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Recently, there has been an increasing interest in searching on the synthesis and optical response characterization of small molecules, in special, those containing organometallic and coordination compounds since these materials play an important role in the development of optoelectronic and photonics devices such as ion selective field effect transistor (ISFET), optical sensors, optical power limiting, all optical switching, holography, photodynamic therapy and so on. Recently, Zn (II) complexes with azomethanes (Schiff bases), benzothiazoles among other heterocycles has been used in several kind of applications, from biology to physics. In all these cases, the chelatogenic cycle (metal-oxygen-nitrogen chain) improves the intramolecular charge transfer (ICT) between the π conjugated arms. This important outcome contributes to the increases of the molecular hyperpolarizability of these compounds potentiating their optical features. Herein, we have investigated the photophysical properties of a new class of salicylidene molecules named N,N'-bis(salicylidene)-1,2-phenylenediamine (salophen) (KG15) and [Zn(salophen)(OH₂)] (KG15/Zn). Salicylidene are Schiff bases-based molecules with potential application in optoelectronic devices. The goal of this study is to show that the Zn (II) coordination complex generate a set of benefic effect that increase strongly the optical hyperpolarizability of this class of organic molecules. To verify this, we studied the influence of Zn (II) on the excited state (ESA) and two-photon absorption (2PA) spectra of a novel salicylidene based molecule employing the white-light pump probe and open-aperture Z-scan techniques. Theoretical calculations were also done in order to describe 2PA allowed electronic transitions and supported our experimental results and to evaluate the possibility of excited state intramolecular proton transfer (ESIPT) process. ACKNOWLEDGMENTS FAPESP, FAPEMIG, CAPES and CNPq are acknowledged.

Revealing the dynamic of excited state proton transfer of a novel π -conjugated salicylidene chromophore

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Excited state intramolecular proton transfer (ESIPT) is a vital event of numerous natural photophysical processes being therefore crucial in chemistry and molecular biology [1]. Due to the transient character of its ground state ESIPT has been used in several applications [2-3]. In the ESIPT electrons are promoted upon photoexcitation to the singlet excited state of the enol form of chromophore. Subsequently the ultrafast ESIPT occurs and the cis-keto form at the singlet excited state is produced which is stabilized by the intramolecular hydrogen bond. Since the ESIPT is much faster than the fluorescence process (radiative decay) the emission observed for the ESIPT chromophores is preferentially due to the keto tautomer [4]. All these processes can be mapped by time-resolved transient absorption spectroscopy. In this context here we report on the ESIPT dynamic of novel salicylidene chromophore (KG21) a compound with potential application in photonic devices. For that we combined the white-light femtosecond pump-probe technique and the Density Functional Theory. Figure 1 shows the excited state dynamics results for the KG21. Figure 1 (a) shows the colormap representing the time- and wavelength-resolved dynamics of the transient absorption spectrum. The excited state absorption (ESA) spectra for different times are displayed in Fig. 1 (b) while Fig. 1 (c) illustrates a decay curve for probe pulse at the peak of ESA band. Figure 1 – (a) ESA colormap representing the time- and wavelength-resolved dynamics of transient absorption spectrum. (b) ESA spectra for different times (0 ps 2.25 ps 8.25 ps and 50 ps). (c) Decay curves for probe pulse tuning at 468 nm. The whole ESA dynamic for the KG21 molecule was modeled employing the rate equation model using the proper energy level diagram. According to this model the cis-enol* form is quickly converted to the hot cis-keto* (hK*) form due to the fast ESIPT process ($\tau_{\text{ESIPT}} = 400$ fs) which is stabilized by the intramolecular hydrogen bond. Subsequently there is the cooling from the hot cis-keto* (hK*) to cold cis-keto* (cK*) state with a characteristic time constant of ~ 35 ps and then the radiative emission from the cis-

keto* tautomer with the maximum emission at 570 nm. These results were confronted and supported by quantum chemical calculations based on the Density Functional Theory.

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