21st I-APS Conference

May 17 - 20, 2011

Mendoza - Argentina

INTER-AMERICAN
PHOTOCHEMICAL SOCIETY

SPONSORS

CONICET

http://www.conicet.gov.ar/

CONICET
INQUIMAE

INIFTA
CONICET
UNLP
FACULTAD DE CIENCIAS EXACTAS
DEPARTAMENTO DE QUIMICA

aaiFQ

ASOCIACION ARGENTINA DE INVESTIGACION FISICOQUIMICA

http://www.aaifq.org.ar/

EDINBURGH
INSTRUMENTS

RENISHAW
apply innovation™

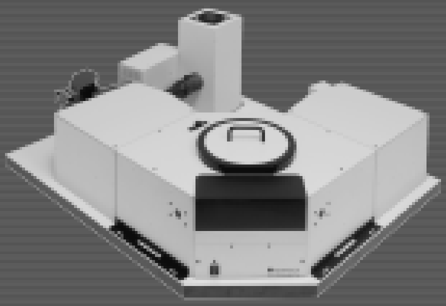
LASEROPTICS

CVI Melles Griot

Buckman

RENISHAW
inVia Raman Microscope
LEICA DMLM

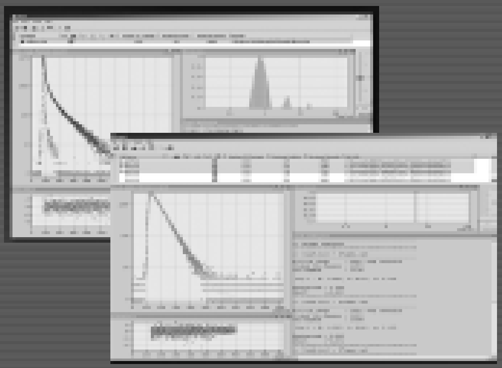
Fluorescence & Phosphorescence Spectrometers



FLSP920 series
Steady state, fluorescence lifetime (utilising TCSPC) and phosphorescence (MCS) decay measurements
Microscope attachment - single molecule applications

Accessories
Temperature control options
Polarisers
Integrating sphere
Pulsed diode lasers and LEDs
Stopped flow system
Platereader
Advanced analysis software (FAST)

Software features – F900
Spectral correction
Fitting of single and multi-exponential decays
Eleven measurement modes including; synchronous spectra, anisotropy spectra and time resolved spectra
Cryostat and peltier cooled sample holder control



FAST - advanced analysis software
Discrete component analysis of multiple exponential terms
Fluorescence lifetime distribution analysis
Global lifetime analysis
Advanced analysis of time resolved fluorescence anisotropy

TCSPC: Time correlated single photon counting, Fluorescence decays: 100 ps – 50 µs
MCS: Multi-Channel Scaling, Phosphorescence decays: 1 µs – 10 s
Steady State Sensitivity (Water Raman SNR): <6000:1

EDINBURGH INSTRUMENTS

A: 2 Bain Square, Kirkton Campus, Livingston, EH54 7DQ, U.K.
T: +44 (0) 1506 425 300
F: +44 (0) 1506 425 320 / 326
E: sales@edinst.com
W: www.edinst.com
www.edinburghinstruments.com

PROGRAM

Tuesday May 17

14.00-17.00		Registration
17.15-17.30		Welcome
17.30-18.10	**L1**	Tito Scaiano (Canada) *Tuning plasmon transitions and their applications in organic photochemistry*
18.10-18.50	**L2**	Fernando Sigoli (Brazil) *Rare earth doped luminescent materials: oxides, complexes and hybrid matrices*
18.50-19.30	**L3**	Alexandre Brolo (Canada) *Plasmonic structures and their applications in biomedicine and enhanced spectroscopy*
20.00-22.00		Conference Reception

Wednesday May 18

08.00-08.30		**Registration**
08.30-09.10	**L4**	Luisa De Cola (Germany) *Luminescent soft and hard assemblies*
09.10-09.50	**L5**	Guillermo Bazán (USA) *Design, synthesis and processing of narrow band gap organic semiconductors for solar cell fabrication*
09.50-10.30	**L6**	Alan Aspuru (USA) *Finding renewable energy materials using one screensaver at a time: Combinatorial quantum chemistry for organic photovoltaics.*
10.30-10.50		Coffee Break
10.50-11.30	**L7**	Claudio Borsarelli (Argentina) *Photochemistry of sensitizers in macromolecular systems: from humic acids to proteins*
11.30-12.10	**L8**	Richard Cogdell (UK) *How purple photosynthetic bacteria harvest solar radiation*
12.10-12.50	**L9**	Linda Johnston (Canada) *Fluorescence imaging on the nanoescale*
13.00-15.30		Lunch
15.30-16.10	**L10**	**Cilento Prize Conference:** María Laura Dántola *Production and quenching of reactive oxygen species by pterin derivatives.*
16.10-16.50	**L11**	Bruno Robert (France) *Molecular basis of photoprotection in photosynthetic organisms*
16.50-17.30	**L12**	James Mc Cusker *Identifying Reaction Coordinates for Ultrafast Excited-state Dynamics.*
17.30-18.00		Coffee Break
18.00-21.00		Poster session 1

Thursday May 19

08.30-09.10	**L13**	**Closs Prize Conference:** Kevin Stamplekoskie *Using the Surface Plasmon Absorption of Silver Nanoparticles to a Maximum.*
09.10-09.50	**L14**	Michael Hoffmann (USA) *Artificial photosynthesis via the photoelectrochemical and photocatalytic reduction of CO_2 with the simultaneous production of H_2*
09.50-10.30	**L15**	Gustavo Argüello (Argentina)
10.30-10.50		Coffee Break
10.50-11.30	**L16**	Daniel Mártire (Argentina) *The employment of humic substances in photochemical experiments. micro- and nano-heterogeneous systems*
11.30-12.10	**L17**	Chad Jafvert (USA) *Sunlight-mediated reactions involving C60 and functionalized single-walled carbon nanotubes in the aquatic environment.*
12.10-12.50	**L18**	Marcelo Gehlen (Brazil) *Photoinduced intramolecular charge-transfer in dyes and in conjugated polymer end-capped with electron acceptor.*
13.00-15.30		Lunch
15.30-16.10	**L19**	Josef Michl (USA) *Designed Singlet Fission as a Possible Tool in Photovoltaics.*
16.10-16.50	**L20**	Richard Weiss (USA) *What controls the fates of pyrenyl singlet states and benzylic triplet radical pairs in the melted and glassy states of poly(alkyl methacrylate)s?*
16.50-17.30	**L21**	Alexis Aspee (Chile) *Photo-induced free radicals for the study of antioxidants behavior in complex biological systems.*
17.30-18.10	**L22**	Sergio Bonesi (Argentina) *Application of Photochemical Reactions in Organic Syntheses. Photo-Fries rearrangement, photoreduction and photooxidation reactions.*
18.10-18.40		Coffee Break
18.40-21.30		Poster session 2

Friday May 20

08.30-09.10	**L23**	Alicia Peñéñory (Argentina) *Photoinduced electron transfer chemistry: mechanism and applications in organochalcogenide synthesis.*
09.10-09.50	**L24**	Carlos Silva (Canada) *The mechanism of efficient charge photogeneration in semicrystalline polymeric semiconductors*
09.50-10.30	**L25**	Dwayner Miller (Canada) *Making the molecular movie": first frames…coming features.*
10.30-10.50		Coffee Break
10.50-11.30	**L26**	Teresa Atvars (Brazil) *Morphology of Polymer Blends in Electroluminescent Devices.*
11.30-12.10	**L27**	Ksenija Glusak (USA) *Photochemical and electrochemical behavior of flavin derivatives.*
12.10-12.50	**L28**	Víctor Batista (USA) *Studies of oxomanganese complexes for natural and artificial photosynthesis*
12.50-15.30		Lunch
15.00-15.40	**L29**	Germán Günther (Chile) *Sucrose Monoesters and microheterogeneous systems.*
15.40-16.20	**L30**	Luis Otero (Argentina) *Development of Supramolecular Dyes with Application in Optoelectronics*.
16.20-17.00	**L31**	Gerald Meyer (USA) *Solar Energy Conversion with Molecules*
17.00-17.30		Coffee Break
17.30-20.30		Poster session 3
21.30		Conference Dinner and party

INVITED TALKS

Tuning Plasmon Transitions and their Applications in Organic Photochemistry

J.C. Scaiano
Department of Chemistry, Centre for Catalysis Research and InnovationUniversity of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

Photochemically generated free radicals can be utilized as reducing agents to produce metal nanoparticles. By controlling growth mechanisms it is possible to select the size and morphology of these particles; further, it is possible to deposit metal nanoparticles on a wide range of supports that effectively ‘tune’ the reactivity of the particles. These particles find applications in catalysis and in photocatalysis.

A molecule irradiated in the proximity of a metal nanoparticle can be viewed as undergoing transmitter/receiver antenna interactions, a process that has also been described as analogous to a lightning rod effect. Thus irradiating the nanoparticle itself can deliver energy to a strategically located organic molecule through plasmon field interactions. While fluorescence and Raman enhancements through these interactions are well established, other forms of plasmon sensitization remain unexplored. For example, we have observed that methylene blue (MB) interacts with aqueous gold nanoparticles (AuNP) leading to enhanced triplet yields and anomalous ultrafast quenching kinetics.

Plasmon interactions can take other forms, such as simple energy delivery through particle localized photothermal effects, electron relay mechanisms that can be used to promote reductions and oxidations and localized polymerization.

Example will be presented of metal nanoparticle catalysis of organic reactions. In the cases of photocatalysis, the results will be compared with other methodologies, including microwave irradiation. The ‘laser drop’ technique will be discussed in the context of a valuable tool to study the mechanisms of plasmon-mediated photocatalysis.

Rare earth doped luminescent materials: oxides, complexes and hybrid matrices

Fernando A. Sigoli

Functional Materials Laboratory - Institute of Chemistry – University of Campinas – UNICAMP – Campinas, São Paulo, Brazil, 13083-970.

The rare earth ions (RE) exhibit interesting luminescent properties due the 4f-4f intraconfiguracional transitions. The degeneration of $4f^n$ orbitals is broken by (i) the high interelectronic repulsion, (ii) by the spin-orbital coupling and (iii) by the ligand field effect that promotes energy difference about 100 cm^{-1} between the electronic levels. Therefore, the choice of the matrices is very important and among the possibilities are (i) inorganic matrixes such as oxide, fluoride and glasses, (i) rare earth complexes and (ii) silicon based hybrid materials. One of the major scope of our research group concern about the investigation of different rare earth-doped matrices suitable for several applications such as optical devices and sensors. Some mechanisms that promotes the intensification of the emission of the rare earth ions such as: metal nanoparticles surface plasmon resonance (SPR) and antenna effect are also been investigated. ZnO is a very interesting material due to its electrical, optical and photochemical properties. However, its use as rare earth matrix is limited due to the rare earth radii and charge. In order to overcome part of these difficulties the expansion of the ZnO crystal cell parameters by doping this semiconductor with sulfur and silver(I) has been used as an strategy. The methodology used for the preparation of sulfur containing-zinc oxide leads to a polydisperse submicrometer aggregates consisting of spherical nanocrystallites and the presence of the Zn-S bonds decreases the ZnO band gap energy probably due to a valence band offset. Luminescent rare earth-doped oxide nanoparticles have been studied for several applications such as: field emission displays and immunoassays. Their luminescent properties have a narrow relationship with particle size, due to the surface emission quenching process. The control of particle sizes and their morphology may be done by a modified homogeneous precipitation method controlling the dielectric constant of the reaction medium. In the rare earth complexes field, the common ligands used are, oxygenated ligands, and nitrogenated ligands such as: β-diketones, and 1,10-phenantroline, respectively. The ligand plays an important influence in the intraconfiguracional transition of the rare earth ions in terms of magnitude, number of lines and ratio of transitions intensities. Their influences can be analyzed using the values of the Judd-Ofelt (JO) intensity parameters that have been widely determined for Eu(III) complexes and for Nd(III), Pr(III) and Sm(III)-doped glasses. Their determination for other rare earth complexes is uncommon. Recently, our group has proposed an useful approach to obtain the JO intensity parameters of Sm(III) complexes using the absorption spectra of rare earth complexes dispersed in KBr pellets. This approach can be applied to other rare earth complexes that have spin allowed transitions and it can be validate by comparing the emission spectra of the complexes (as a powder) with those dispersed in KBr pellets. Concerning the ligands properties, we have calculated the energy of the triplet state of a series of ligands such as: beta-diketones and carbolixilic acids. The calculated energies agree very well with the experimental ones allowing the corrected choice of the rare earth ions in order to have an efficient antenna effect. In the field of silicon based hybrid materials our research group has been working with functionalization of silicones such as polymethylsiloxane (PDMS). The phosphine oxide molecules are anchored on the silicone surface by hydrossililation reactions and the P=O group has been used to bind rare earth complexes containing aqua ligands which are exchanged by the P=O group modifying the emission spectra as well the life times. The main objective of the last strategy is the preparation of thin films of rare earth containing-silicones that can be applied to electroluminescent devices.

Plasmonic Materials for Biosensing and Enhanced Spectroscopy

A. G. Brolo
Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, V8W 3V6, Canada

Nanostructured metallic surfaces support surface plasmon (SP) excitations. The resonance conditions depend on the optical properties at the metal-dielectric interface, and the monitoring of the shift of the surface plasmon resonance (SPR) due to molecular adsorption events is a well established approach in biosensing. The SPR condition also leads to an enhancement in the electric field at the surface which can be explore for enhanced spectroscopy schemes, such as surface-enhanced Raman scattering (SERS).

In this work, we will provide an overview of the recent advances from our group on the fabrication of gold nanostructures, by both nanolithographic and self-assembly methods, and discuss some of their applications to biomedical relevant problems. These plasmonic platforms are suitable for miniaturization and integration in microfluidics and fiber optics-based devices.

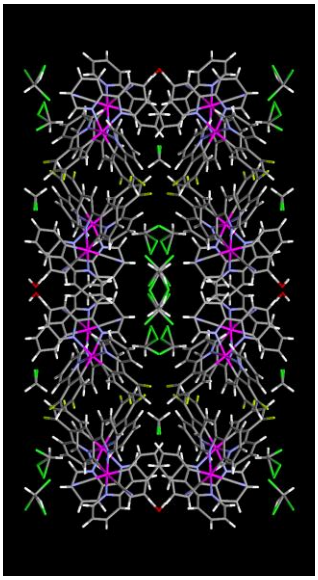
Arrays of nanoholes on thin gold films are one of the plasmonic devices that we explored. These arrays were prepared by focused ion beam milling and integrated into microfluidic devices as biosensing elements. These nanostructures are being explored for detection of cancer markers in serological fluids. The idea is to develop an assay capable of detecting several cancer-specific (ovarian and prostate) antibodies simultaneously and in real time. Results from plasmonic substrates prepared by the self assembly of gold nanoparticles on flat surfaces will also be presented. These structures presented strong SERS and a relationship between the fabrication parameters and the SERS signal was obtained. Microarrays of self assembled nanoparticles were prepared and preliminary results indicated that this platform is a good candidate for ultrasensitive multiplex biosensing schemes based on SERS. The integration of plasmonics into optical fiber tips was explored for remote sensing. The concept provides the basis for the application of bioplasmonics in endoscopy. We will also discuss the application of plasmonics in cell imaging.

LUMINESCENT SOFT AND HARD ASSEMBLIES

Noviyan Darmavan, Matteo Mauro, Luisa De Cola
Physikalisches Institut, and CeNTech, University of Münster, Mendelstrasse, D-48149 Muenster (decola@uni-muenster.de)

Electroluminescent metal complexes have been widely investigated for their potential use as dopant in Organig Light Emitting Devices, OLEDs, and when charged in Light Emitting Electrochemical Cells, LEECs. In this we will discuss the formation of soft [1,2] and hard crystalline luminescent systems [3-5]. Tuning the design of the metal complexes based mainly on iridium and platinum metal ions and containing phenylpyridine, pyridine, and pyridine azoles, or dinegative tridentate N-N-N ligands we are able to control the degree of intermolecular interactions leading to the formation of fibers and gels, or crystalline materials. In particular the possibility to promote aggregation and the new emission properties rising from the formation of the assemblies, such as enhancement of the emission, will be discussed in two examples.

A non-luminescent platinum complex, becoming extremely emitting (90% emission quantum yields) upon aggregation, is described. The Pt(II) complex can assemble in fibers or even form luminescent gels. The material has been used to construct electroluminescent devices [1]. The aggregation can also be prevented and other neutral Pt(II) complexes have been prepared and used for OLED materials.



Finally crystalline iridium complexes (left figure) will be discussed and porous structures have been obtained with some of them. In particular, in one of the described systems, two luminescent iridium complexes, possessing different emission colors, and complementary charges are employed to form complex salts and non covalent linked crystalline porous photo- and electroactive framework [3]. The strategy described can be extended to many photo- and electroresponsive ionic transition metal complexes and could constitute the future generation of organometallic zeolite-like structures. The modulation of their properties with appropriate guests will be then discussed.

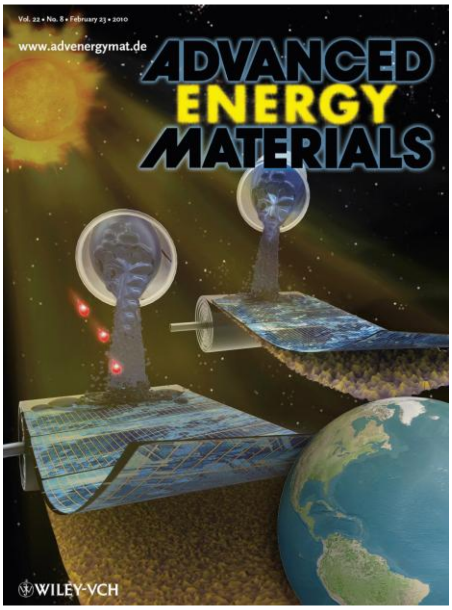
[1] C. A. Strassert, C.-H. Chien, M. D. Galvez Lopez, D. Kourkoulos, D. Hertel, K. Meerholz, L. De Cola *Angew. Chem. Int. Ed.,* **2011**, *50*, 946.
[2] M. Mydlak, M. Mauro, F. Polo, M. Felicetti, J. Leonhardt, G. Diener, L. De Cola, C.A. Strassert submitted.
[3] M. Mauro, K. C. Schuermann, R. Prétôt, A. Hafner, P. Mercandelli, A. Sironi, L. De Cola *Angew. Chem. Int. Ed.,* **2010**, *49,* 1222.
[4] N. Darmawan, R. Fröhlich, L. De Cola, submitted.
[5] E. Quartapelle Procopio, M. Mauro, M. Panigati, D. Donghi, P. Mercandelli, A. Sironi, G. D´Alfonso, L. De Cola *J. Am. Chem. Soc.,* **2010**, *132,* 14397.

Design, Synthesis and Processing of Narrow Band Gap Organic Semiconductors for Solar Cell Fabrication

Guillermo Bazan, Greg Welch, James Rogers, Louis Perez, Jason Azoulay, Xuan-Dung Dang, Minhong Tong, Ed Kramer, Thuc-Quyen Nguyen and Alan Heeter
Center for Polymers and Organic Solids, University of California, Santa Barbara,
California 93106, USA

High charge separation efficiency combined with the reduced fabrication costs associated with solution processing (printing and coating) and the potential for implementation on flexible substrates make “plastic” solar cells a compelling option for the next generation of photovoltaic devices. The control the donor/acceptor blend morphology in bulk heterojunction materials as required for achieving high power conversion efficiency is therefore of primary concern. We showed that by incorporating a few volume percent of high boiling point solvent additive, the power conversion efficiency of photovoltaic cells (AM 1.5 conditions) is substantially increased, and this method of optimization is now the most widely used processing option for polymeric systems.

Subsequent efforts have centered on understanding the mechanism of action of the additives and this will be discussed in some detail. This work involves understanding in detail how film morphology evolves as a function of time and under different conditions.



More recently, the improved synthesis of polymers has been studied, in particular those backbone systems that lead to aggregation in solution and high performance devices. We will present polymerization procedures that lead to high molecular weight product in short reaction times and involve simple purification protocols. Emerging structure/function relationships will be examined, as well as those conjugated polymer systems that allow fabrication of devices that have power conversion efficiencies at 6 %.

Lastly, we will examine a new class of small molecules with modular features that can be used to fine tune the optical absorption to match the solar spectrum, molecular orbital energies that are appropriate to achieve excellent power conversion efficiencies and topological attributes for controlling phase separation and film forming behavior. Solar cell optimization requires a set of processing options different from those that are found most useful in the case of conjugated polymers. A comparison of the merits for both classes of materials will also be made.

Finding renewable energy materials using one screensaver at a time: Combinatorial quantum chemistry for organic photovoltaics

Alán Aspuru-Guzik
Department of Chemistry and Chemical Biology
Harvard University 12 Oxford Street, Room M113, Cambridge, MA 02138
E-mail: aspuru@chemistry.harvard.edu

During this talk, I will describe our group's efforts in the Clean Energy Project (http://cleanenergy.harvard.edu) , a collaboration with the IBM World Community Grid to search for novel materials for organic photovoltaics and organic electronics using computational resources from volunteer donors around the world. Our project aims to find new materials using techniques from ab initio quantum chemistry combined with cheminformatics tools that are usually employed for the discovery of novel pharmaceutical compounds. To date, we have computed more than a million structures using first-principles methods, and have analyzed three million using cheminformatics. I will describe our progress so far, and describe immediate goals. A computationally-predicted material with an unusually high hole mobility of 13 cm2/Vs was synthesized by Zhenan Bao's group at Stanford. I will describe this experimental collaboration as well.

Photochemistry of Sensitizers in Macromolecular Systems: from Humic Acids to Proteins

Claudio D. Borsarelli
Instituto de Química del NOA (INQUINOA-CONICET). Universidad Nacional de Santiago del Estero, Av. Belgrano (S) 1912. 4200 – Sgo. del Estero, Argentina. E-mail: cborsarelli@yahoo.com.ar

Many photochemical processes of interest involve the interaction of sensitizer molecules with natural and artificial macromolecules, which ranging from humic substances, edible polymers, synthetic polyelectrolytes, and proteins, among others.

Depending on the nature of the macromolecules, different types of interactions (e.g. hydrophobic, electrostatic, hydrogen-bonding, etc.) with the sensitizer can modify drastically the photophysical deactivation pathways of the sensitizer and/or the reactivity of their excited states with the macromolecule, inducing structural and conformational changes of the macromolecule such as its breakdown, cross linking, oxidation, etc.

In this talk, we will discuss the photochemistry of some systems of sensitizer-macromolecule studied in our laboratory during the last years, including dyes molecules such as Rose Bengal and Methylene Blue associated to humic acids, or Eosinol with a synthetic thymine-based polyelectrolytes; interaction of Riboflavin with the edible glycoprotein Gum Arabic, and Ruthenium (II) trisbipyridine complex in the presence of proteins.

For each system, it will be discussed the features of the photosensitization process, e.g. photobleaching, photooxidation, photocrosslinking, etc. Depending on the studied system, the interpretation of these results can be applied to several photochemical areas, such as those related with environmental, food, technology or biology.

How purple photosynthetic bacteria harvest solar energy

Richard J. Cogdell
Institute of Molecular, Cell and Systems Biology, College of Medical, Veterinary and Life Sciences, University of Glasgow, Glasgow G12 8QQ,

The light harvesting system of purple photosynthetic bacteria is now very well understood, both structurally and functionally (1). It consists of two types of light harvesting complexes, called LH1 and LH2, which are each made up of oligomers of alpha/beta apoprotein dimers. Each dimer non-covalently binds bacteriochlorophyll and carotenoid molecules. Light is usually absorbed by LH2 and then the excitation energy is transferred via LH1 to the reaction centre, where it is used to drive a trans-membrane charge separation reaction. Figure 1 shows a cartoon representation of how these components are organised relative to each other in the photosynthetic membrane.

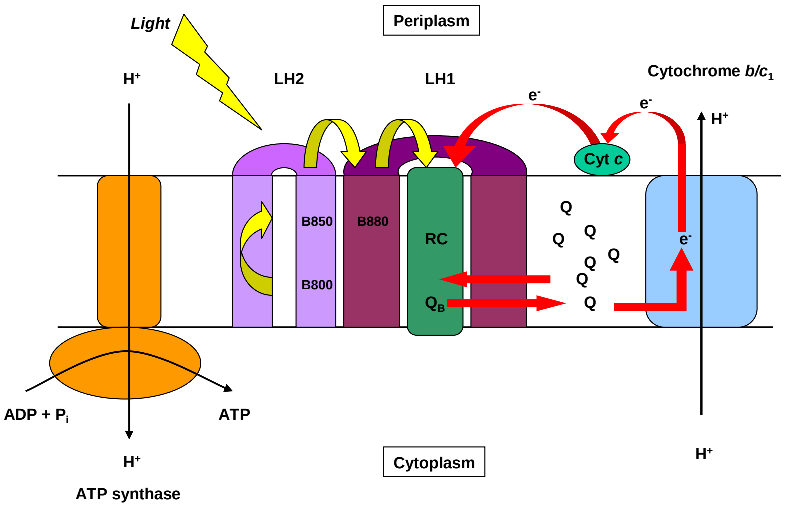


Figure 1. A diagrammatic representation of the organisation of the light harvesting system in purple bacterial membranes

This presentation will describe in detail the structure and function of the LH1 and LH2 complexes. The pathways of energy transfer from LH2 to the reaction centre will be presented from fs out to longer times.

1. Cogdell, R. J., Gall, A., and Kohler, J. 2006, The architecture and function of the light-harvesting apparatus of purple bacteria: from single molecules to *in vivo* membranes Quarterly Reviews of Biophysics 39, 3, 227-324

Fluorescence Imaging on the Nanoscale

Linda J. Johnston
Steacie Institute for Molecular Sciences, National Research Council of Canada,
Ottawa, Ontario K1A 0R6

Advanced imaging tools that provide nanometer-scale spatial resolution and high sensitivity (to the single molecule level) are required to visualize biological processes at the molecular level. One approach to address this challenge involves the development of integrated, multimodal techniques that employ various combinations of scanning probe microscopy and fluorescence spectroscopy and microscopy. The availability of several contrast mechanisms on the same microscope platform facilitates functional, correlated imaging and molecular-level characterization of biological assemblies. These techniques combine the ability to image individual molecules and to probe molecular interactions by atomic force spectroscopy with the advantages of fluorescence microscopy for the selective and specific visualization of labeled molecules down to the single molecule level and for monitoring dynamics in live cells. Correlated multi-modal imaging techniques have significant potential for cell biology research, for new clinical diagnosis tools and for assay development for high content screening. These approaches will be illustrated using several recent examples from our group that focus on probing the assembly of plasma membrane signalling complexes, developing assays for correlating DNA probe binding with chromosome structure and investigating lipid-peptide interactions in supported bilayers membranes.

Production and quenching of reactive oxygen species by pterin derivatives

<u>Maria Laura Dántola</u>,[1] Mariana Vignoni,[1] Franco Cabrerizo,[2] Esther Oliveros,[3] Andrés H. Thomas[1] and Carolina Lorente[1]

[1]*INIFTA, Dep. De Química, Fac. Ciencias Exactas, Universidad Nacional de La Plata, CONICET. Casilla de Correo 16, Sucursal 4, (1900) La Plata, Argentina. e-mail:ldantola@inifta.unlp.edu.ar*

[2]*IIB-INTECH, Universidad Nacional de San Martín, CONICET. Camino Circunv. Laguna Km 6. CC 164 (7130) Chascomús, Argentina.*

[3]*Laboratoire des IMRCP, UMR CNRS/UPS 5623, Université Paul Sabatier (Toulouse III), 118 route de Narbonne, F-31062 Toulouse cédex 9, France.*

Pterins, a family of heterocyclic compounds derived from 2-aminopteridin-4(1*H*)-one, are widespread in living systems and participate in important biological functions, such as metabolic redox processes. Under UV-A excitation (320–400 nm), aromatic pterins (Pt) can generate reactive oxygen species (ROS), as a consequence of both energy and electron transfer processes from their triplet excited state. Quantum yields of singlet oxygen production depend largely on the nature of the substituents on the pterin moiety and on the pH.[1,2] Formation of the superoxide anion by electron transfer between the Pt radical anion and molecular oxygen leads to the production of significant amounts of H_2O_2 by disproportionation.[3] Dihydropterins (H_2Pt) do not produce singlet oxygen but are oxidized by this species with high rate constants yielding Pt as well as H_2O_2.[4] In contrast to aromatic derivatives, H_2Pt are oxidized by H_2O_2, and rates and products strongly depend on the nature of the substituents on the H_2Pt moiety.[5] Aromatic pterins have been found *in vivo* under pathological conditions, *e.g.* biopterin or 6-carboxypterin are present in the skin of patients affected by vitiligo, a depigmentation disorder. The biomedical implications of the production of ROS by pterin derivatives and their reactivity with these species are discussed.

[1] Andrés H. Thomas, Carolina Lorente, Alberto L. Capparelli, Claudia G. Martínez, André M. Braun and Esther Oliveros, *Photochem. Photobiol. Sci.*, 2003, 2, 245–250.

[2] Franco M. Cabrerizo, M. Laura Dántola, Gabriela Petroselli, Alberto L. Capparelli, Andrés H. Thomas, André M. Braun, Carolina Lorente and Esther Oliveros, *Photochem. Photobiol.*, 2007, 83, 526–534.

[3] M. Laura Dántola, Mariana Vignoni, Constanza González, Carolina Lorente, Patricia Vicendo, Esther Oliveros and Andrés H. Thomas, *Free Radic. Biol. Med.*, 2010, 49 (6), 1014-1022.

[4] M. Laura Dántola, Andrés H. Thomas, André M. Braun, Esther Oliveros and Carolina Lorente, *J. Phys. Chem. A, 2007,* 111, 4280-4288.

[5] M. Laura Dántola, Tobias M.Schuler, M. Paula Denofrio, Mariana Vignoni, Alberto L. Capparelli, Carolina Lorente and Andrés H. Thomas, *Tetrahedron*, 2008, 64, 8692-8699.

Molecular Basis of Photoprotection in Photosynthetic Organisms

Bruno Robert
Institute of Biology and Technology CEA Saclay, 91191 Gif/Yvette Cedex. France
bruno.robert@cea.fr

Through their light-harvesting antenna, plants frequently absorb more solar energy than they can use in photosynthesis. This excess energy has the potential to cause cell damage, such as pigment bleaching and protein inactivation. To minimise photodamage, a number of protection mechanisms exist, which we have characterized at a molecular/functional level. I will discuss the following mechanisms in the light of our most recent results

Protection against singlet oxygen production by chlorophyll triplet states

We recently showed that in most light-harvesting proteins of oxygenic organisms, the pigment organization dramatically modify the properties of the chlorophyll triplet states, in order to minimize the production of singlet oxygen. I will report the excitation energy cascade in these complexes, and how we can acess to the structure of these triplet states.

Protection against photooxidative stress induces by high light environments

Excitation energy quenchers rapidly appear in the photosynthetic membrane of plants and algae when these organisms are exposed to high illumination conditions. Until recently, this mechanism was still poorly understood. In the last years, combined use of advanced spectroscopic methods, first applied on isolated light-harvesting complexes then developed for their application on systems as complicated as whole leaves, have yielded a precise picture of the molecular events which underlie this important mechanism of photoprotection in higher plants. I will report recent results on diatoms which suggest that the photoprotection mechanisms are quite similar in these algae, although the structure of their light-harvesting apparatus is quite different.

Identifying Reaction Coordinates for Ultrafast Excited-state Dynamics

James K. McCusker
Department of Chemistry, Michigan State University, East Lansing, MI 48824 USA

Experimental methods for examining the photo-induced properties of systems on femtosecond time scales have the potential to provide unprecedented insights into the mechanistic details by which molecules capture and redistribute absorbed energy; over the past decade, a variety of probes ranging from optical to resonance Raman to x-ray have been developed toward this end. Unlike ground-state recovery, however, whose dynamics can be reasonably predicted and/or rationalized within the context of models such as the Energy Gap Law, there exists no analogous conceptual framework for processes occurring during the course of excited-state evolution (i.e., relaxation from the Franck-Condon state to the lowest-energy excited state of the molecule). The situation is particularly difficult for transition metal-containing systems, which do not appear to adhere to any of the commonly held guidelines concerning the relative rates of various processes that have traditional been of use for interpreting the excite-state dynamics of some (but by no means all) classes of organic chromophores.

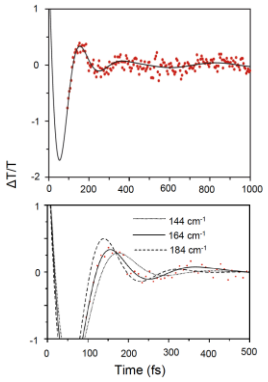


Figure 1. Time-resolved transient absorption data for $Cr(acac)_3$ in a CH_3CN solution at 605 nm following excitation at 600 nm. The upper plot shows a fit of the experimental data to a damped 164 cm^{-1} oscillation, whereas the lower plot shows fits to other frequencies, suggesting a value of 165 ± 20 cm^{-1} is appropriate. Adapted from reference 2.

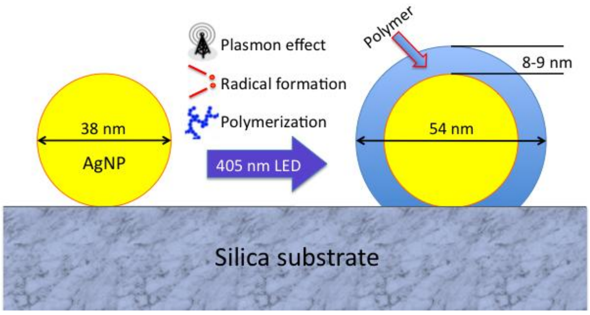
As part of our effort to understand the ultrafast excited-state dynamics of metal complexes, we have been exploring the extent to which a combination of femtosecond spectroscopy and synthetic design can be used to begin developing guidelines for identifying (and ultimately exploiting) reaction coordinates that underlie excited-state evolution in transition metal-based chromophores. This presentation will focus on results from two efforts in our group. The first deals with the excited-state dynamics of Cr(III) complexes. Such systems are of interest for a number of reasons, not the least of which is their relative simplicity in terms of electronic structure. Building off of earlier work in our group that served to define a lower-limit for the time scale of intersystem crossing to the ^2E ligand-field excited state in $Cr(acac)_3$,[1] we have carried out sub-50 fs time-resolved studies that resulted in the observation of vibrational coherence associated with the excited-state evolution of this compound (Figure 1).[2] An analysis of these data led to a hypothesis as to the identity of the vibrational mode(s) driving the ISC process and the synthesis of related compounds designed around these coordinates; the results of ultrafast optical studies of these systems will be described. The second area deals with complexes of Fe(II) which we are exploring in the context of developing chromophores of the first transition series for use in dye-sensitized solar cells. Recent results concerning the time scale and mechanism of charge transfer-state relaxation in such compounds, the interplay between these dynamics and geometric structure, as well as the application of femtosecond time-resolved x-ray absorption[3] and resonance Raman[4] spectroscopies to the study of their excited-state evolution will be discussed.

References:
[1] Juban, E.A.; McCusker, J.K. *J. Am. Chem. Soc.* **2005**, *127*, 6857-6865.
[2] Schrauben, J.N.; Dillman, K.; Beck, W.F.; McCusker, J.K. *Chem. Sci.* **2010**, *1*, 405-410.
[3] Huse, N.; Cho, H.; Hong, K.; Kim, T.K.; Jamula, L.; de Groot, F.M.F.; McCusker, J.K.; Schoenlein, R.W. *J. Phys. Chem. Lett.*, in press.
[4] Smeigh, A.L.; Creelman, M.; Mathies, R.A.; McCusker, J.K. *J. Am. Chem. Soc.* **2008**, *130*, 14105-14107.

Using the Surface Plasmon Absorption of Silver Nanoparticles to a Maximum

Kevin Stamplecoskie, **Juan (Tito) Scaiano**
Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada.

Resent research in the Scaiano lab has had a strong focus on exploiting the plasmon absorption of metal nanoparticles, specifically Au, Ag and Cu. Of the noble metals, silver nanoparticles (AgNP) possess a particularly intense local electromagnetic field generated around the particles when they are excited by light. Presented here are several examples of how this induced electromagnetic field has been used in some of our most resent work. For example, excitation of the plasmon of small AgNP (~3 nm) has been used to control/synthesize various shapes of AgNP. AgNP have also been used to enhance the Raman signal of molecules bound to the AgNP surface, with a focus on determining the best size and shape of particles to maximize the Raman signal. The surface plasmon of AgNP has also been excited in order to enhance photochemistry of molecules in the near vicinity of the particles. The last example of enhancing photochemistry near AgNP has implications for photolithography with the possibility of generating lithographic features drastically below the diffraction limit of the light used, and with feature sizes smaller than those generated by current top-down photolithography techniques.



Artificial Photosynthesis via the Photoelectrochemical and Photocatalytic Reduction of CO_2 with the Simultaneous Production of H_2

Michael R. Hoffmann, Jina Choi, and Sinbed Ou
W. M. Keck Laboratories, California Institute of Technology, Pasadena, CA 91125 USA

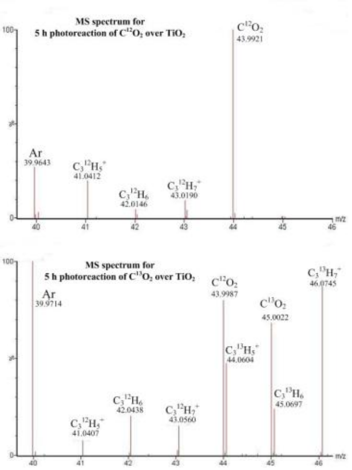
Over the past decade, there has been a renaissance of interest in the artificial photo-fixation of carbon dioxide due to concerns about global warming and the renewed interest in the development of over non-fossil fuel sources of energy. Thus, there has been a resurgence of research into electrochemical and photochemical CO_2 fixation and conversion into energy rich products. Simple metal electrodes including copper and zinc have been employed for the electrochemical CO_2 reduction. In addition, semiconductor electrodes based on CdS, GaP, InP and GaAs and many others have been used for the photo-electrochemical reduction of CO_2. In our lab, we have explored several different electrode and photocatalyst combinations that could be used and readily prepared on a large-scale at relatively low cost. In one approach, a photo-electrochemical cell, which consists of anodes prepared on Ti metal base supports, is prepared by coating successive layers of various mixed-metal, semiconducting oxides onto the Ti base with the top layer consisting of Bi-doped TiO_2 and coupled with either naked metal cathodes or various semiconductor-coated metal counter-electrodes. In alternative approach, we have employed functionalized TiO_2 nanotube arrays synthesized directly on to Ti-base metal electrodes.

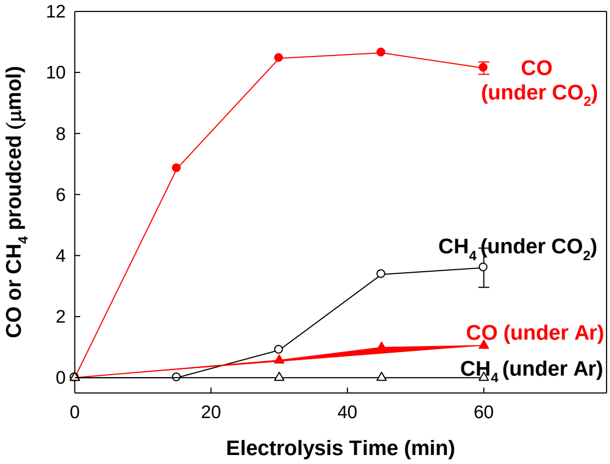
Using these systems and similar photocatalytic systems, we have observed that depending on the specific solution-phase or electrolytic conditions that CO_2 is reduced to CO, HCOOH, HCHO, CH_3OH and CH_4 either electrochemically or photocatalytically. We also have isotopic-labeling evidence of the conversion of CO_2 to higher molecular weight hydrocarbons via a photocatalytic Fischer-Tropsch reactions involving further CO reduction. At the same time there is a competition for electrons by protons and water resulting in the simultaneous formation of H_2.

$$CO_2 + H_2O \rightarrow CO + H_2O_2$$

$$CO_2 + 2\ H_2O \rightarrow HCOOH + H_2O_2$$

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$





Gas-phase photochemistry. Laboratory studies of peroxynitrates.

Gustavo Argüello

INFIQC-Dpto de Físico Química, Fac. de Cs. Qcas, Universidad Nacional de Córdoba, Argentina.

Synthetic and mechanistic studies have been carried out to characterize some peroxynitrates that could form in the atmosphere as a consequence of the atmospheric degradation of precursor compounds that have found widespread use in many applications.

Distinction between alkyl and acyl peroxynitrates is presented through the analysis of the photolysis of $C_2F_5C(O)Cl$ in the presence of O_2 and NO_2.

The kinetics and mechanisms of photooxidation initiated by chlorine atoms in the presence of NO_2 will be analyzed for 2-ethyl hexanol, 2-ethyl hexanal and ethyl formate that lead to the formation of PAN, PPN as well as $C_2H_5OC(O)OONO_2$.

In all cases, the experimental set-up comprises mainly FTIR spectroscopy to follow the course of reaction using a standard IR glass cell or a long-path optical cell and irradiating with either λ=254 or λ=360 nm UV radiation.

The employment of humic substances in photochemical experiments. Micro-and nano-heterogeneous systems

Daniel Mártire
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CONICET, Universidad Nacional de La Plata, La Plata, Argentina. E-mail: dmartire@inifta.unlp.edu.ar

Humic substances (HS) are the major organic constituents of soil and aquatic environments and therefore play an important role in influencing fate and transport of colloidal particles. Photolysis of HS leads to the formation of several reactive species including hydrated electrons, reactive triplet states, hydroxyl radicals, singlet molecular oxygen, superoxide, and hydrogen peroxide, all of which play a role in aquatic photochemistry.

The effect of the presence of humic acids (HA) on the photodegradation of a mixture of emerging pollutants commonly present in natural waters is discussed. For this purpose, the chosen pollutants were acetominophene (analgesic), caffeine (stimulating agent), acetemiprid (pesticide), clofibric acid (fungicide), carbamazepine (psychiatric drug) and amoxycilin (antibiotic).

The effect of HA aggregate formation on the photosensitized generation and subsequent quenching of singlet molecular oxygen $O_2(a^1\Delta_g)$ was also investigated. Time-resolved $O_2(a^1\Delta_g)$ phosphorescence traces were obtained from (a) bulk samples of HA dispersions and (b) microscope-based experiments performed upon irradiation of a single HA aggregate. In the bulk experiments, the dependence of the $O_2(a^1\Delta_g)$ lifetime on the HA concentration yields a critical concentration for the formation of micrometric HA aggregates of 0.58 g L^{-1}. This value is consistent with that obtained using pyrene as a fluorescent probe (0.38 g L^{-1}). Microscope-based experiments were also performed with HA samples containing added singlet oxygen sensitizers; either the hydrophobic meso-tetraphenylporphyrin (TPP) or the hydrophilic 5,10,15,20-tetrakis(N-methyl-4-pyridyl)-21H,23H-porphine (TMPyP). Singlet oxygen phosphorescence could only be detected upon irradiation of TMPyP, a molecule which localizes on the exterior part of the HA aggregates. The inability to detect $O_2(a^1\Delta_g)$ phosphorescence from HA samples containing TPP is consistent with the model that the $O_2(a^1\Delta_g)$ produced in the interior of the aggregate was completely quenched by the high local concentration of HA reactive groups in this environment

Magnetite (Fe_3O_4) nanoparticles have recently attracted widespread attention because of their unique properties, including high surface-to-volume ratio, high chemical reactivity, and supermagnetism. Bare magnetite nanoparticles are very much susceptible to air oxidation and are easily aggregated in aqueous systems. Thus, the stabilization of the iron oxide particles is necessary. Recent research showed that humic acid has high affinity to Fe_3O_4 nanoparticles, and sorption of HA on the Fe_3O_4 nanoparticles enhances the stability of nanodispersions by preventing their aggregation. We prepared HA-coated magnetite nanoparticles and compared the photogeneration of reactive species by these particles to those of the HA employed as stabilizers.

Sunlight-Mediated Reactions Involving C_{60} and Functionalized Single-Walled Carbon Nanotubes in the Aquatic Environment

Chad T. Jafvert[1], **Ching-Ying Chen**[1,2], **Wen-Che Hou**[1,3]
[1]*Purdue University, West Lafayette, IN USA;* [2]*current address: Connecticut Experimental Station, New Haven, CT USA;* [3]*current address: College of Engineering, University of Arizona, Tempe, AZ US*

Release of fullerene nanomaterials to the environment is inevitable due to their anticipated production rates as indicated by the growing number of commercial products that contain them. Therefore, to construct accurate risk assessment models for these materials (to determine if regulated production is warranted), there is an urgent need for information on their reactivity (or conversely persistence) and transformation pathways in the natural environment. Because of their size, the initial environmental transformation reactions of fullerene materials (including nC_{60} nanoparticles) are likely to be dominated by abiotic oxidative and extracellular microbial processes, with photochemical transformation a likely important abiotic fate process. To this end, over the past few years we have been examining the photochemical reactivity of fullerene materials in aqueous media.

Buckminsterfullerene (C_{60}) is a spherical molecule with a diameter of 7Ǻ and has a very low water solubility of ~3-8 ng/L. However, it forms colloidal nano-aggregates in water that have diameters in the hundreds of nanometers, with these aggregated generally referred to as nC_{60}. When dissolved in organic solvents in molecular form, and under light within the solar spectrum, several research groups have shown that excited-state C_{60} can transfer energy to ground state O_2 producing singlet oxygen ($^1O_2$), which in term reacts with $^3C_{60}$ to form epoxides. We have shown that aqueous colloidal dispersions of nC_{60} also generate $^1O_2$ in sunlight, with concurrent loss of C_{60} over a period of days. Phototransformation products include more water soluble species. The FTIR spectrum of sunlight-irradiated nC_{60} reveals the complete loss of the sharp absorption peaks of the parent C_{60} and appearance of new absorption bands at frequencies consistent with C–O stretching (1060 cm^{-1}); C–O–H in-plane bending and/or carboxylate asymmetric stretching (1390 cm^{-1}); and C=C stretching and/or carboxylate symmetric stretching (1600 cm^{-1}).

Interpreting results of similar experiments conducted with carboxylated single-walled carbon nanotubes (SWNT-COOH) is complicated by the fact that essentially all preparations of SWNTs are contaminated with metal species (used as catalysts during their production) and amorphous carbon, at total impurity concentrations of 1-10%, with some of these impurities residing within the nanotubes. However, surface defects in the conjugated π-bond surface (due to functionalization with the carboxyl groups) are anticipated to increase photoreactivity compared to unfunctionalized nanotubes. Further, due to functionalization, aqueous dispersions of as-received SWNT-COOH are easily prepared by mild sonication. Irradiation with sunlight produces $^1O_2$, superoxide anion ($O_2^{\cdot -}$), and hydroxyl radicals (·OH), as determined by loss of respective ROS scavengers (over a period of a few days). Through a series of experiments using SWNT-COOH treated to remove some of the impurities and/or by added metal-chelating agents, we show that nickel (the major metal impurity within our material) contributes to the production of $O_2^{\cdot -}$ and ·OH, but not to $^1O_2$ production. Future experiments are planned in which we will examine changes in nanotube surface chemistry upon sunlight exposure.

Photoinduced intramolecular charge-transfer in dyes and in conjugated polymer end-capped with electron acceptor

Marcelo H. Gehlen
Instituto de Química de São Carlos – Universidade de São Paulo
13566-590 – São Carlos – SP – Brasil

Fluorescent dyes with photoinduced intramolecular charge-transfer (ICT) process driven by β-enaminone group capable to form resonance assisted hydrogen bond (RAHB) structure were prepared from aromatic and heterocyclic precursor molecules such as 1-aminopyrene, 9-amino acridine, and adenine. The electronic ground and excited-state spectral properties of these new dyes are modulated by type of substituent in the β-enaminone group and solvent interaction as well. The excited-state properties and the complex kinetics observed are results of the interplay between charge and proton transfer, together with the presence of possible conformers or tautomers associated with the keto-amine/enol-imine equilibrium. The applications of such dye derivatives as molecular probes in radical copolymerization with acrylic monomers and as reporters in silver nanoparticles dye interaction in solution are also discussed. Dyes with only RAHB effect are used to follow hydrolase activity. In the final part, the process of intrachain energy migration to weak charge-transfer state in polyfluorene end-capped with naphthalimide derivative is used to calculate the rate of energy hopping in the conjugated polymer structure.

Designed Singlet Fission as a Possible Tool in Photovoltaics

Justin C. Johnson,[1] Akin Akdag,[2] Millie B. Smith,[2] Alexandre Olive,[2] Brian R. Stepp,[2,3] Arthur J. Nozik,[1] Zdeněk Havlas,[3] and Josef Michl[2,3]
[1]National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, CO 80401,
[2]Department of Chemistry and Biochemistry, University of Colorado, 215 UCB, Boulder, CO 80309-0215, [3]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

Singlet fission is a process in which a singlet excited molecule shares it energy with a ground state neighbor to produce the triplet excited state of each. Its efficiency is usually only a few per cent because of competition by other processes such as vibrational relaxation. Although the triplet pair is initially born coupled into an overall singlet, making singlet fission spin allowed and potentially as fast as other forms of internal conversion, spin dipole-dipole interaction terms in the Hamiltonian can rapidly convert the singlet coupled pair into into a triplet or a quintet pair. Further spin-allowed processes can then lead to intramolecularly excited triplet or quintet species, hence singlet fission has some features in common with intersystem crossing, too.

Singlet fission is of interest in photovoltaics because it offers the opportunity to use a single photon of sufficient energy to produce two electron-hole pairs, thus increasing the photocurrent. The maximum theoretical efficiency would be increased by a factor of 1.5 if the triplet yield were 200% and if they all produced usable charge separation events. Our goal is the development of design rules that will permit the synthesis of absorbers that convert singlets to triplets with 200% efficiency. The task is divided into (i) selection of monomeric chromophores conducive to isoergic or slightly exoergic singlet fission, (ii) choice of inter-chromophore coupling in dimers, oligomers, polymers, aggregates, or crystals that induces rapid singlet fission. The structural guidance that has been developed so far has already permitted us to attain a triplet yield of 200 ± 30% in a thin layer of neat 1,3-diphenylisobenzofuran, designed for the purpose.

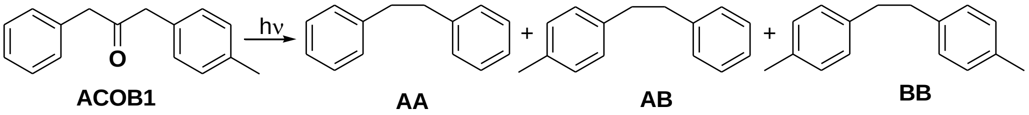
1. Smith, M. B.; Michl, J. “Singlet Fission”, *Chem. Rev.* **2010**, *110*, 6891.

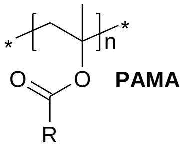
What Controls the Fates of Pyrenyl Singlet States and Benzylic Triplet Radical Pairs in the Melted and Glassy States of Poly(alkyl methacrylate)s?

Shibu Abraham,[1] Indrajit Ghosh,[2] Werner M. Nau,[2] Carlos A. Chesta,[3] Steven J. Pas,[4] Anita J. Hill[4] and Richard G. Weiss[1]
[1]*Department of Chemistry, Georgetown University, Washington, DC 20057-1227, USA, (email: weissr@georgetown.edu);* [2]*Jacobs University Bremen, School of Science & Engineering, D-28759 Bremen, Germany;* [3]*Departamento de Química, Universidad Nacional de Río Cuarto, 5800-Río Cuarto, Argentina;* [4]*CSIRO Manufacturing and Materials Technology, Private Bag 33, Clayton MDC, Vic 3169, Australia.*

Changes in the static and dynamic fluorescence of pyrene (**PyH**) and *N*-alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-amine (**PyC3NMeR**) and in Norrish I photoreactions of 1-(4-methylphenyl)-3-phenyl-2-propanone (**ACOB1**) have been used to probe structural and morphological properties of a series of poly(alkyl methacrylate)s (**PAMA**, where alkyl is ethyl, butyl, isobutyl, cyclohexyl, and hexadecyl) below and above their glass (or melting) transition temperatures. These **PAMA** have been selected because they cover a wide range of glass transition temperatures and structure types. The I_1/I_3 fluorescence intensity ratios from **PyH** and the photophysical properties of the intramolecular exciplexes from the **PyC3NMeR** have been employed to locate the probes within the polymer matrices and to assess their microviscosities.[1] The ratio of in-cage to the sum of in-cage and out-of-cage recombinations of the triplet benzylic radical-pairs generated upon irradiation of **ACOB1** (F_c) have been calculated from relative photoproduct yields and used to assess the influence of the hosts on radical escape from cavities and diffusion through the bulk. It is found that the probes prefer to reside near the ester groups of the polymer backbones and the radical combination pathways are controlled principally by chain relaxation rates of the **PAMA** rather than their hole free volume (as measured by positron annihilation spectroscopy). This leads to unanticipated and subtle changes of F_c as a function **PAMA** phase (temperature) and alkyl group. The results will be compared with those from our previous work in which polyethylenes with differing degrees of crystallinity, where hole free volume was the principal factor controlling F_c.[2]

We thank the U.S. National Science Foundation for its support of this research.





$$\boxed{F_c = \frac{[\mathbf{AB}] - [\mathbf{AA}] - [\mathbf{BB}]}{[\mathbf{AB}] + [\mathbf{AA}] + [\mathbf{BB}]}}$$

(1) Abraham, S.; Atvars, T. D. Z.; Weiss, R. G. *J. Phys. Chem.* **2010**, *114*, 12221-12233.
(2) Chesta, C. A.; Mohanty, J.; Nau, W. M.; Bhattacharjee, U.; Weiss, R. G. *J. Am. Chem. Soc.* **2007**, *129*, 5012-5022.

Photo-induced free radicals for the study of antioxidants behavior in complex biological systems

Alexis Aspée
Universidad de Santiago de Chile, Facultad de Química y Biología, Casilla 40 Correo 33 Santiago, Chile. Email: alexis.aspee@usach.cl

In the last few years, our research group has employed stable free radicals such as galvinoxyl and nitroxide prefluorescent probes for evaluating accessibility and environmental parameters that could influence the reactivity of antioxidants with free radicals in complex media such as cell membranes and proteins. In this context, the development of photochemical techniques able to efficiently produce free radicals in specific locations would be of great relevance to study secondary free radical processes such as free radical migration and/or antioxidant role in these complex systems.

In the present work, we have explored the formation of free radicals derived from coumarin 314 (C_{314}) and pyranine (PyOH) induced by laser excitation at visible wavelengths, and determined kinetic rate constants of their reaction with antioxidants by using nanosecond time resolved spectroscopy. In particular, fluorescence and triplet quantum yields and singlet oxygen quantum yield of C_{314} were measured in benzene, acetonitrile, dichloromethane and 10 mM phosphate buffer pH 7.0. Interestingly, C_{314} triplet excited state was detected in benzene with a maximum absorption at 550 nm and a mono-exponential decay of 90 μs lifetime; while laser excitation of C_{314} in aqueous solutions mainly produced a long-lived intermediate (≈160 μs), which showed an intense absorption in the UVA (≈ 370 nm) unaffected by the presence of oxygen. Quenching experiments carried out in aqueous solutions using sodium azide, methyl viologen, deoxyguanosine and tryptophan pointed out into cation radical behavior for this intermediate ($C_{314}^{+\bullet}$). Moreover, computational calculations indicate that *ca.* 40% $C_{314}^{+\bullet}$ spin density is localized on the nitrogen atom, which is compatible with the lack of reactivity toward oxygen mentioned above. On the other hand, laser pulse excitation of PyOH aqueous solutions (phosphate buffer, pH 7.0) by using either 355 nm or 470 nm under anaerobic conditions conducts to the formation of $PyO^{\bullet}$ and $PyO^{\bullet-}$ radicals with absorption maxima centered at 450 and 510 nm, respectively, and also detectable by electron paramagnetic resonance. Additionally, measurements carried out under oxygen saturated and N_2O saturated solutions showed a $PyO^{\bullet}$ radical non reactive toward oxygen, which is fully compatible with spin density calculations. Finally, bimolecular rate constants close to diffusion limit control in water for the quenching of $C_{314}^{+\bullet}$ by phenolic antioxidants would suggest the role of ionic pairs in the reaction mechanism. Interestingly, $PyO^{\bullet}$ radical was several magnitude orders less reactive than $C_{314}^{+\bullet}$ toward antioxidants, fact that could be explained in terms of electrostatic repulsion produced by the three sulfonate groups in PyOH.

The financial support from FONDECYT projects 1085177 and 1110809 are gratefully acknowledged.

Application of Photochemical Reactions in Organic Syntheses. Photo-Fries rearrangement, photoreduction and photooxidation reactions

Sergio M. Bonesi
CIHIDECAR – CONICET, Dep. de Química Orgánica, Fac.de Ciencias Exactas y Naturales, UBA, Pabellón II, 3er Piso, Ciudad Universitaria, Buenos Aires, Argentina.

Photochemical reactions are seldom considered in organic synthesis, whereas thermal methods tend to be preferred and widely diffused. Yet photochemical reactions are clean, easy to perform at ambient temperature and require no harsh conditions and no catalyst such as Lewis acids. Application of the photo-Fries rearrangement reaction to the synthesis of the chroman-4-one ring system is an interesting example. This ring system can be formed in a one–pot fashion under base catalysis starting from a convenient substituted ester where new C–C and C–O bonds are formed simultaneously. Two processes occur consecutively: (1) the photo–Fries rearrangement providing the *o*-hydroxyphenone intermediate and, (2) an intra-molecular *oxa*–Michael cyclization reaction that gives the desired chroman-4-one (reaction 1). Moreover, the method can be used in the synthesis of 4-quinolones under neutral conditions starting from substituted amides. In this case, C–C and C–N bonds are formed simultaneously.

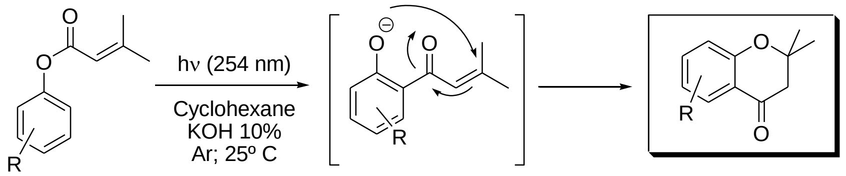
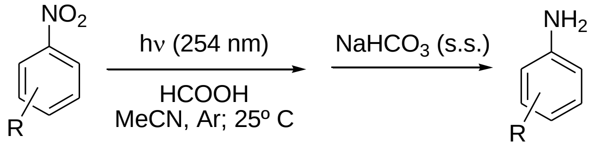


Photo-Fries rearrangement ***Intramolecular oxa-Michael addition*** (1)

Another interesting example in the application of photochemical reactions in organic synthesis is the photoreduction of nitro-arenes. Nitro compounds are important building blocks in organic synthesis and routinely serve as precursors to amines. Among thermal methods that involve hydrogenation and hydride reductions, the formic acid–mediated photo-reduction of nitro-arenes is an alternative process that can be carried out in acetonitrile at ambient temperature, to yield the amine in high yield in short time and with wide functional group tolerance. In addition, the photoreduction is equally efficient in the reactions of poly-cyclic and heterocyclic nitro-arenes. This photochemical reaction is initiated by a photo-induced electron transfer (PET) reaction wherein charge transfer that follows excitation yields the nitro-arene radical anion and the formyl radical (reaction 2).



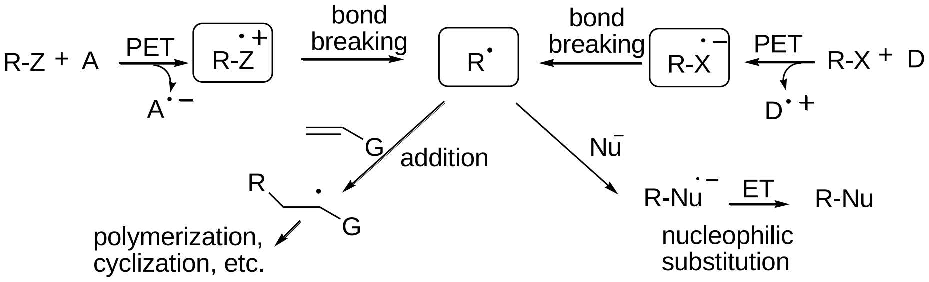
(2)

Photooxidation is yet an alternative oxidation method for sulfides. It is known that dye-sensitized oxidation of alkyl and aryl sulfides give the sulfoxide as the main photoproduct. However, photosensitized oxidation of benzyl sulfides can give selectively the corresponding aldehyde/ketone or the expected sulfoxide under mild conditions, depending on the protic nature of the solvent. Thus, the use of benzene or acetonitrile as solvents provides the carbonyl derivative, whereas methanol yields the sulfoxide as the main photoproduct. The key step for the oxidative C–S bond cleavage appears to be H transfer from the activated α position (benzylic position) in the first intermediate formed, *viz.*, the persulfoxide.

Photoinduced Electron Transfer Chemistry: Mechanism and Applications in Organochalcogenide Synthesis

Alicia B. Peñéñory
INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba, Córdoba, Argentina, penenory@fcq.unc.edu.ar

Photoinduced electron transfer (PET) reactions have become a useful tool in organic synthesis since difficult or unattainable transformations with more conventional organic reactions can be easily performed. In the first step of such a reaction, a radical ion pair is generated showing typical reactivities. Frequently, bond breaking leading to proton exchange or elimination of an ion subsequently affords neutral radicals. In the context of radical chemistry, these reactions are particularly valuable since they offer an easy access to radical species without using toxic reagents such as tin derivatives. At present, the use of radical reactions for the synthesis of target organic compounds is widely recognized and many studies describe the synthetic applications of different radical procedures.[1] Among them, the radical nucleophilic substitution by the $S_{RN}1$ mechanism has proven to be a versatile procedure to form new Carbon-Carbon and Carbon-heteroatom bonds. In addition, cyclization reactions of radicals leading to carbocyclic and heterocyclic compounds have been successfully applied to the synthesis of natural products.[2]



We have studied oxidative or reductive photoinduced electron transfer process to render primarily radical cations or radical anions, respectively, involving chalcogenide species and their reactivities. In the present communication, the synthesis of different aryl alkyl and diaryl sulphides,[3] aryl methyl selenides,[4] benzothiazoles,[5] etc. will be discussed emphasizing the mechanism and the reactive intermediates involved.[6]

References

[1]. *Radicals in Organic Synthesis*, Renaud P.; M. P. Sibi, M. P., Eds. Wiley-VCH: Weinheim, Germany, 2001.

[2] a) Peñéñory, A. B. and Argüello, J. E. in In *Handbook of Synthetic Photochemistry*, (Eds: A. Albini, M. Fagnoni), Wiley & Sons: **2010**; Chapter 10, pp 319. b) Rossi, R. A.; Peñéñory, A. B. *Current Organic Synthesis*, **2006**, *3*, 121-158.

[3] (a) Argüello, J. E.; Schmidt, L. C.; Peñéñory, A. B. *Org. Lett.* **2003**, *5*, 4133-4136. (b) Argüello, J. E.; Schmidt, L. C.; Peñéñory, A. B. *Arkivoc* **2003,** Part (x) 411-419. (c) Schmidt, L. C.; Rey, V.; Peñéñory, A. B. *Eur. J. Org. Chem.* **2006**, 2210-2214. (d) Schmidt, L. C.; Argüello, J. E.; Peñéñory A. B. *J. Org. Chem.* **2007**, *72*, 2936-2944.

[4] Bouchet, L.; Peñéñory, A. B.; Argüello, J. E. *Tet. Lett.* **2011**, asap.

[5] Rey, V.; Soria-Castro, S, M.; Argüello, J. E. Peñéñory, A. B.; *Tet. Lett.* **2009**, *50*, 4720-4723.

[6] Rey, V.; Pierini, A.B.; Peñéñory, A. B. *J. Org. Chem.* **2009**, *74*, 1223-1230.

The mechanism of efficient charge photogeneration in semicrystalline polymeric semiconductors

Francis Paquin[1], Gianluca Latini[2], Maciej Sakowicz[1], Paul-Ludovic Karsenti[1], Natalie Stinglein[2], and Carlos Silva[1]
[1]*Département de physique et Regroupement québécois sur les matériaux de pointe, Université de Montréal, C.P. 6128, Succursale centre-ville, Montréal H3C 3J7, Canada*
[2]*Department of Materials and Centre for Plastic Electronics, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*

Unravelling primary electronic processes as a function of film microstructure in films of semiconductor polymers opens a fundamental window to their materials physics, which is of central importance for emerging applications in optoelectronics. Primary photoexcitations in π-conjugated polymers are Frenkel excitons, for which a binding energy 0.3–0.5 eV must be overcome in order to produce electrons and holes. At room temperature, this energy is much higher than lattice thermal energies, so charge separation must be achieved extrinsically by doping the film with electron acceptors such as fullerene derivatives to fabricate charge-transfer heterostructures. Here, we focus on charge generation and recombination dynamics in neat regioregular poly(3-hexylthiophene) (P3HT), a model polymeric semiconductor. It adopts π-stacked lamellar microstructures in the solid state, leading to two-dimensional electronic dispersion. The degree of crystallinity induced by molecular organization has a profound influence on electronic properties; a specific example is the high yield (η) of apparently direct charge photogeneration in P3HT. Whereas $\eta \ll 1\%$ in polymeric semiconductors [1], various groups have reported η up to 30% over ultrafast timescales in P3HT films at room temperature [2–7]. This is very surprising because photoemission spectroscopy measurements place the energy of charge-transfer states 0.3 eV above the singlet exciton in neat regioregular P3HT [8]. Weak interchain electronic coupling in the lamellar architecture leads to a free-exciton bandwidth – the pure electronic bandwidth due to dispersion of π electrons neglecting coupling to vibrations – that are well below this energy offset [9], so direct charge generation ought to be improbable. Considering this, two fundamental questions arise: (i) what is the mechanism of prompt charge photogeneration in P3HT? (ii) What is the role of microstructure in defining it?

Here, we implement time-resolved photoluminescence (PL) spectroscopy at 10 K to probe charge photogeneration and recombination dynamics. We find that charge generation occurs continuously over sub-nanosecond timescales, but not by diffusion-limited exciton dissociation. Rather, we conclude that it occurs by dissociation of excitons localized at interfaces between conformationally ordered (aggregate) and disordered (non-aggregate) domains, driven by energetic disorder. Thus, prompt charge photogeneration is an *extrinsic* process, and film microstructure determines the surface area of interfaces between domains.

[1] C. Silva et al., J. Phys.: Condens. Mat., 14, 9803 (2002).
[2] E. Hendry et al., Phys. Rev. Lett., 92, 196601 (2004).
[3] X. Ai et al., J. Phys. Chem. B, 110, 25462 (2006).
[4] C. Sheng et al., Phys. Rev. B, 75, 085206 (2007).
[5] P. D. Cunningham and L. M. Hayden, J. Phys. Chem. C, 112, 7928 (2008).
[6] J. Piris et al., J. Phys. Chem. C, 113, 14500 (2009).
[7] W. J. Grzegorczyk et al., J. Phys. Chem. C, 114, 5182 (2010).
[8] C. Deibel et al., Phys. Rev. B, 81, 085202 (2010).
[9] F. C. Spano, J. Chem. Phys., 122, 234701 (2005); 126, 159901 (2007).

“Making the Molecular Movie”: First Frames…Coming Features

R. J. Dwayne Miller,[1,2]
1. Max Planck Group for Atomically Resolved Dynamics, Department of Physics, University of Hamburg, The Centre for Free Electron Laser Science, DESY, Notkestrasse 8, Hamburg, GERMANY, 22607
2. Department of Chemistry and Physics, University of Toronto, 80 St. George Street,Toronto CANADA, M5S 1H6

One of the great dream experiments in Science is to watch atomic motions as they occur during structural changes. In the fields of chemistry and biology, this prospect provides a direct observation of the very essence of chemistry and the central unifying concept of transition states in structural transitions. From a physics perspective, this capability would enable observation of rarified states of matter at an atomic level of inspection, with similar important consequences for understanding nonequilibrium dynamics and collective phenomena. This experiment has been referred to as "making the molecular movie". Due to the extraordinary requirements for simultaneous spatial and temporal resolution, it was thought to be an impossible quest and has been previously discussed in the context of the purest form of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been finally realized (Siwick et al. Science 2003). Previously thought intractable problems in attaining sufficient brightness and spatial resolution, with respect to the inherent electron-electron repulsion or space charge broadening, has been solved. With this new level of acuity in observing structural dynamics, there have been many surprises and this will be an underlying theme. Several movies depicting atomic motions during passage through structural transitions relevant to condensed phase dynamics will be shown (Sciaini et al. Nature, 2009, Ernstorfer et al. Science 2009, Eichberger et al Nature 2010). The primitive origin of molecular cooperativity has also been discovered in recent studies of molecular crystals. These new developments will be discussed in the context of developing the necessary technology to directly observe the structure-function correlation in biomolecules — the fundamental molecular basis of biological systems. The future is even brighter with the advent of a new concept in relativistic electron guns that will open up direct observation of atomic motions in solution phase to gas phase systems with femtosecond time resolution to watch even the fastest atomic motions. Some of the important scientific problems to be addressed with ultrabright electron sources will be discussed to give an impression of the potential impact of this emerging field.

Morphology of Polymer Blends in Electroluminescent Devices

Leni Akcelrud[1] and Teresa D. Z. Atvars[2]
[1]Departamento de Química, Universidade Federal do Paraná, Centro Politécnico,
Caixa Postal 19081, 81531-990 Curitiba, PR, Brasil *Institute of Chemistry,*
[2]*Universidade Estadual de Campinas – UNICAMP, P.O. Box 6154, Campinas,*
13084-971, SP, Brazil, e-mail: tatvars@iqm.unicamp.br

Conducting polymers are one example of materials frequently used as an active media for electroluminescent and photovoltaic devices because of their electrical and optical properties as well as their good thermal and photochemical stabilities. They are materials that offer several possibilities of processability using different deposition technologies for small and large areas, on rigid or flexible substrates. To improve the performance of electroluminescent devices, polymer blends are frequently used at least as a proof of concept. The greater performance is attributed to the presence of bulk heterojunction, which is a consequence of the phase separation process. Here we present some examples in devices using polymer blends with inert/active materials and with all active polymers and we discuss differences in the photoluminescence (PL) and electroluminescence (EL) emissions based on the morphology of the materials. For example, blends composed by blue emitter and matrix host poly(9,9-dihexyl-2,7-fluorene) (PF-1), and the green and red emitters poly[(9,9-dihexyl-9H-fluorene-2,7-diyl)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl] (PF-2) and poly[2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV) respectively, as guests components with compositions of PF-1:PF-2:MEH-PPV = 100:0.01:0.20 (w/w) and PF-1:P(MMA-*co*-MMAnt):PF-2:MEH-PPV = 100:40:0.01:0.20 (w/w) have different performance and white emissions can be observed for the EL but not for the PL. In other example, blend composed by a copolymer of polyfluorene-PPV and polyvinyl carbazol showed an efficient exciton migration from the host (PVK) to the guest (PDHFPPV) resulting in both PL and EL emissions coming from solely PDHFPPV. In all cases the morphology is interfering with both the PL and the EL but in different ways.

Acknowledgements: Author thanks FAPESP, CNPq and INEO/FAPESP/CNPq for financial supports and fellowships and several of my collaborators.

Photochemical and Electrochemical Behavior of Flavin Derivatives

Ksenija D. Glusac, Ekaterina Mirzakulova, Renat Khatmullin, Dapeng Zhou
Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403

We present a study of two series of flavin derivatives. The first series involves natural flavin cofactors, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). We used femtosecond pump probe spectroscopy to study the effect of adenine moiety on the excitedstate behaviour of FAD in several oxidation and protonation states. We further investigated the effect of adenine moiety on the light-induced repair of thymidine dimers. This study revealed some interesting aspects of natural DNA repair by a flavoprotein DNA Photolyase. In our model compounds, we find that the thymine dimer repair becomes more efficient in the adenine-containing cofactors, possibly by facilitating a two-step electron transfer process.

The second class of model compounds involves N(5)-ethylflavinium ion (Et-Fl$^+$) and its pseudobase (Et-FlOH). These compounds are model systems for bacterial bioluminescence. Our group's interest in Et-Fl$^+$ is due to its potential for catalytic water oxidation. We found that the anodic oxidation of Et-Fl$^+$ at +2 V leads to the catalytic release of oxygen from water. Spectroelectrochemical measurements suggest that the catalytic cycle involves a pseudobase intermediate, Et-FlOH radical cation. We present a series of electrochemical and pump-probe experiments on Et-Fl$^+$ and Et-FlOH and discuss the possible mechanism of water oxidation catalysis.
catalysis.

Studies of Oxomanganese Complexes for Natural and Artificial Photosynthesis

Sandra Luber, Ivan Rivalta and Victor S. Batista
Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520

Mechanistic investigations of the water-splitting reaction of the oxygen-evolving complex (OEC) of photosystem II (PSII) are fundamentally informed by structural studies of oxomanganese complexes. Many physical techniques have provided important insights into the OEC structure and function, including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy as well as mass spectrometry (MS), electron paramagnetic resonance (EPR) spectroscopy, and Fourier transform infrared spectroscopy applied in conjunction with mutagenesis studies. However, experimental studies have yet to yield consensus as to the exact configuration of the catalytic metal cluster and its ligation scheme. Computational modeling studies, including density functional (DFT) theory combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods for explicitly including the influence of the surrounding protein, have proposed chemically satisfactory models of the fully ligated OEC within PSII that are maximally consistent with experimental results. The inorganic core of these models is similar to the crystallographic model upon which they were based, but comprises important modifications due to structural refinement, hydration, and proteinaceous ligation which improve agreement with a wide range of experimental data. The computational models are useful for rationalizing spectroscopic and crystallographic results and for building a complete structure-based mechanism of water-splitting as described by the intermediate oxidation states of oxomanganese complexes. This talk summarizes recent advances on studies of the OEC of PSII and biomimetic oxomanganese complexes for artificial photosynthesis.

Sucrose Monoesters and microheterogeneous systems

Germán Günther
Laboratorio de Cinética y Fotoquímica, Facultad de Ciencias Químicas y Farmacéuticas,
Universidad de Chile, Santiago, Chile

Non-ionic surfactants have shown to be a successful alternative for non-biological origin commonly used detergents. A particularly interesting group of surfactants are the fatty acid esters of monosaccharides and disaccharides, and among them sucrose fatty acid esters (SFAE). This kind of surfactants has 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)

The raw materials involved in their synthesis are low cost, simple, effortlessly accessible and renewable (independent from the petrochemical industry). SFAE 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 and to extract specific compounds (i.e. enzymes, receptors and transport carriers), and can also be removed by simple dialysis.

However, due to the difficulties to obtain and purify sucrose monoesters, only a limited number of studies on the physico-chemical properties (on normal micelles and reverse micelles) have been carried out with pure compounds. Currently, mixtures of mono and polyesters, or mixtures of several monoesters are being used. In these mixtures, such as the WASAG® series, the hydrophobicity is controlled by varying the length of the alkyl chains and the proportion of mono- and polyesters. The presence of the bulky and highly hydroxylated sucrose head, confers an important degree of structuration to the water near the bilayer, this situation can be very relevant in the interface of the microestructures formed, especially in the case of the small water pools of reversed micelles.

To characterize physical chemically the different microheterogeneous aggregates formed by SFAE (micelles and reversed micelles), different photophysical and photochemical procedures were employed.

Additionally considering that solubilization of biological membranes by detergents has long been used as the main method for the isolation and purification of membrane proteins and other constituents, the capacity of solubilization of SFAE on several synthetic membranes (with and without cholesterol) and erytrocites were studied. Also the blocking effect of the presence of the sucrose moieties on the surface of bilayers was studied, monitoring the remotion of cholesterol by cyclodextrin and HDL particles.

Financial support from Fondecyt 1040573-1080412

Development of Supramolecular Dyes with Application in Optoelectronics

Luis Otero
Departamento de Química. Universidad Nacional de Río Cuarto. Agencia Postal 3. 5800 Río Cuarto. Argentina. e-mail: lotero@exa.unrc.edu.ar

The development of new organic materials with applications in electro-optical devices is one of the most active fields of research in the last years. The continuous growing of worldwide requirements of environmental friendly energy sources has led to a greater increment in the research for new solar energy conversion devices. In this frame, dye-sensitized solar cells (DSSCs) is a research area of great interested around the world. A crucial issue in DSSC design is the used dye. Until now, Ru(II) polypyridyl complexes still dominated the most successful systems. However, the limited availability and environmental issues could limit the extensive applications of Ru-based DSSCs. Furthermore, Ru-based dyes are expensive and hard to purify as compared to organic sensitizers. Thus, the search of new highly efficient dyes is one of the most active research subjects in DSSCs development. Organic dyes exhibit many advantages, such as the huge diversity of molecular structures and the possibility of obtaining materials at relatively low cost. Moreover, organic dyes normally exhibit high molar extinction coefficients as compared to those of Ru dyes (< 20 000 M-1 cm-1), allowing to use thinner nano-structured oxide semiconductor films with comparable light-harvesting efficiency, a key factor in solid-state DSSC development.

On the other hand, the use of organic polymers in electronic and optoelectronic holds the advantages to obtain large area flexible devices, replacing rigid Si and glass substrates. It is expected that the use of polymers will introduce a significantly advance in the construction and application of devices for energy generation, image display, lighting systems and others. The improvement and application of flexible devices are directly associated to the development of new suitable materials and deposition processes. At present two major approaches are used to deposit optoelectronic organic materials layers: thermal evaporation and solution processing. Although thermal evaporation through the use of mask can produce well-ordered patterned films, the throughput is slow and involves expensive vacuum systems. Also, thermal evaporation demands materials with sublimation capability and excellent thermal stability, properties that are not easy to obtain in polymers. On the other hand, low-cost solution processes, as spin coating, deep coating and drop coating, usually produce non-patterned films that cover the entire substrate. A promising technique for conducting polymer film production is the electropolymerization of electroactive monomers. The polymer films made through this way is an alternative and attractive film formation method to build highly efficient optoelectronic devices.

The formation and characterization of a series of polymer films with optoelectronic properties obtained by electropolymerization will be show. Polymers containing porphyrins, a powerful optical and redox active center, were synthesized and analyzed in our laboratory. Furthermore, polymers with electron donor-acceptor moieties, linked by fluorene centre were developed and applied in electro-optical devices.

Solar Energy Conversion with Molecules

Byron Farnum, John Rowley, and Gerald. J. Meyer
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA

Photo-initiated reactions that form chemical bonds are important for the conversion and storage of solar energy. Iodide photo-oxidation yields the I-I bonds present in $I_2^{-\bullet}$ and I_3^- but the detailed mechanism(s) remain speculative. Here we present evidence that metal-to-ligand charge transfer (MLCT) excited states can be used to facilitate the formation and breaking of I-I bonds. Early attempts to sensitize iodide oxidation to visible light with the MLCT excited states of $Ru(bpy)_3^{2+}$ in aqueous solution revealed inefficient excited state electron transfer. This presumably resulted from the very positive $E^o(I^\bullet/I^-)$ reduction potential, $Ru(bpy)_3^{2+}*$ was simply not a strong enough oxidant.Indeed, Ru(II) compounds based on 2,2'-bipyrazine (bpz), which are potent photo-oxidants, were efficiently quenched by iodide in acetonitrile. Evidence that this quenching results in iodide oxidation to the iodine atom has recently been reported utilizing $Ru(bpz)_2(deeb)^{2+*}$ as the photooxidant, **Reaction 1.** In these studies, the MLCT excited state of $Ru(bpz)_2(deeb)^{2+}$ ($E^o(Ru^{2+*/+})$ = 1.6 V vs. NHE) was quenched by iodide in acetonitrile by a purely dynamic process with a rate constant very close to that expected for a diffusion limited reaction, 6.6 x 10^{10} M^{-1} s^{-1}. The growth of reduced ruthenium compound, $Ru(bpz^-)(bpz)(deeb)^+$, monitored by transient absorption was quantified with an equal rate constant, indicating it was a primary photoproduct.

$$\boldsymbol{Ru(bpz)_2(deeb)^{2+*} + I^- \rightarrow Ru(bpz^-)(bpz)(deeb)^+ + I^\bullet} \qquad \textbf{(1)}$$

Diiodide was observed secondary to the growth of $Ru(bpz^-)(bpz)(deeb)^+$ with a rate constant three times slower, k = 2.4 x 10^{10} M^{-1} s^{-1}, indicating that it was not a primary photoproduct. This observation was in accord with the initial formation of an iodine atom that subsequently reacted with iodide to form the I-I bond of $I_2^{\bullet-}$. It is of note that excited state electron transfer was near quantitative but the yield of $Ru(bpz^-)(bpz)(deeb)^+$ and $I_2^{\bullet-}$ was low, behavior attributed to a low cage escape yield, ϕ_{CE} = 0.042. Nonetheless, the sensitized photo-oxidation of iodide to iodine atoms with visible light yields I-I bonds in the form of $I_2^{\bullet-}$. We note also that the mechanism for I-I bond formation discovered here is distinctly different from the observed in our previous work using ion-pairs in low dielectric solvents. Reactivity of both $I_2^{\bullet-}$ and I_3^- by the reduced ruthenium compound, $Ru(deeb^-)(deeb)_2^+$, generated by the conventional flash-quench technique were quantified. In the flash-quench experiment, iodide oxidation of $Ru(deeb)_3^{2+*}$ generated $Ru(deeb^-)(deeb)_2^+$, where reaction with $I_2^{\bullet-}$ or I_3^- could be quantified. Titration of I_3^- into solution allowed its reduction to be the predominate pathway. Transient absorption data confirmed that $I_2^{\bullet-}$ was a product of triiodide reduction. Kinetic analysis for the loss of $Ru(deeb^-)(deeb)_2^+$ and I_3^-, and the growth of $I_2^{\bullet-}$ revealed a linear dependence of the observed rate constant with triiodide concentration and yielded a self consistent second-order rate constant of 5.1 x 10^9 M^{-1} s^{-1} for the reduction of I_3^-. Sutin's description of Marcus theory in the context of diffusional bimolecular reactions allowed the reduction potential to be calculated, $E^o(I_3^-/(\ I_2^{\bullet-},\ I^-))$ = -0.34 V *vs.* NHE. In calculating this reduction potential a reorganization energy (λ = 1.0 eV) and pre-exponential factor ($\nu_n\kappa_{el}$ = 10^{11} s^{-1}) were assumed. This data provided the first experimental estimate for the one-electron triiodide reduction potential and showed that it was very negative.

Taken together, these studies provide a strategy for making chemical bonds with visible light while at the same time preventing back reactions that accompany bon-breaking.

ABSTRACTS

1st Poster session

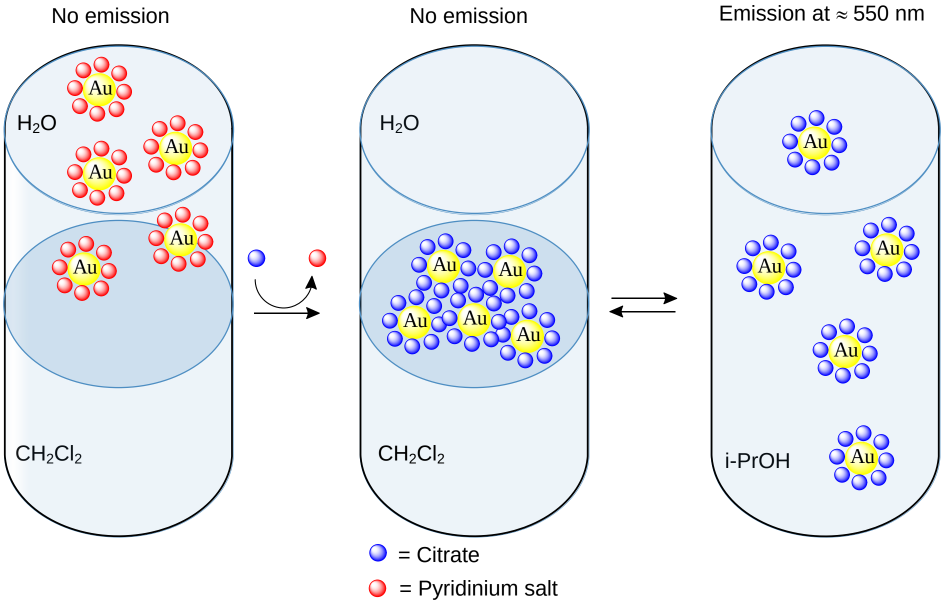
Wednesday May 18

Red shifted fluorescent gold nanoparticles doped with pyridinium salt

Cristian Tirapegui, Juan F. Silva, Carolina Adura, Cristian Vera, Luis Lemus and Carolina Aliaga

Facultad de Química y Biología, Universidad de Santiago de Chile

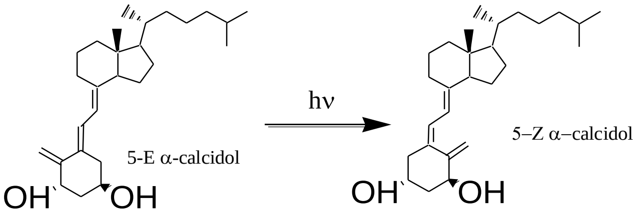
Fluorescent gold nanoparticles doped with a fluorescent pyridinium were prepared by the classical method of $HAuCl_4$ reduction with sodium citrate and subsequent replacement of the tricarboxylate by 1 - (4-mercaptophenyl)-4-phenyl-2,6-di (thien-2 -yl) pyridinium perchlorate. The pseudosphere nanoparticles obtained show a large bathochromic shift (ca 90 nm) in absorption and emission maxima compared to the fluorophore in solution. Also, it was developed a method based on spectrophotometric measurements for obtaining the average number of molecules of the fluorescent pyridinium salt linked to the nanoparticle surface. We tuned the size distribution of nanoparticles according to the tetrachloroauric acid reduction time. We characterized the fluorescent nanoparticles by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and light scattering, spectroscopy fluorescence, and UV-vis.



Photosensitized E-Z isomerization of α-Calcidol. A photochemical chain reaction

Gastón Ariel Estruch, Pedro F. Aramendía
INQUIMAE and Dept. Química Inorgánica, Analítica y Química Física. Facultad de Ciencias Exactas y Naturales. Universidad de Buenos Aires. Pabellón 2. Ciudad Universitaria. 1428 Buenos Aires. Argentina. pedro@qi.fcen.uba.ar

Biologically and in industry, vitamin D and its derivatives are produced photochemically by pericyclic and photoinduced isomerisation reactions. The first reaction involves the ring aperture in the C9-C10 bond of the 7-dehydrocholesterol, present in animal skin. This ring aperture is followed by photosensitized E-Z isomerisation to produce the biologically active compound for human use. Industrially, the production of hydroxylated vitamin D derivatives, such as Vitamin D3 is a pharmaceutically relevant process, producing high added value products. Precursors are extracts from vegetal origin but bearing mainly an E geometry in the 5,6 double bond. Some years ago, Calverley informed the synthesis of vitamin D3 (5-E-α calcidol) with the correct stereochemistry in the Z 5,6 double bond from the E isomer using anthracene and triethylamine (TEA) as the sensitizer system.[1]



Irradiation of E-calcidol with anthracene only in deoxygenated solution yields the Z isomer in a ca 5% yield in the photostationary state. When TEA is added to the system, the E-Z reaction is not inhibited by oxygen any more, the quantum yield of photosiomerization to the Z isomer grows linearly with [E-calcidol], while conversions higher than 90% to the Z isomer are reached in the photostationary state and E-Z quantum yields as high as 45 at [E-calcidol] = 25 mM are reached.

If TEA is replaced by DABCO, the reaction rate drops to 1/3 at the same amine concentration. The observations can be explained by the following mechanism, known as quantum chain reaction

$$\mathrm{An} + h\upsilon \longrightarrow {}^{1}\mathrm{An}$$

$${}^{1}\mathrm{An} \longrightarrow \mathrm{An} + h\upsilon_{f}$$

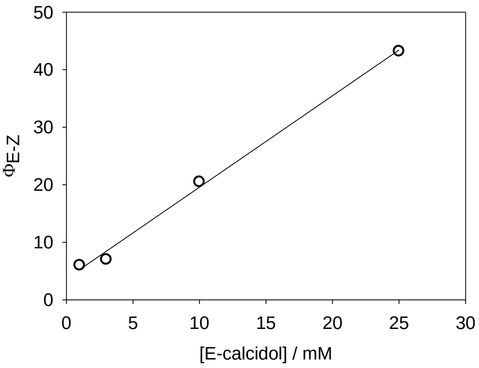
$${}^{1}\mathrm{An} \longrightarrow {}^{3}\mathrm{An}$$

$${}^{1}\mathrm{An} + \mathrm{TEA} \longrightarrow \mathrm{TEA}^{+\cdot} + \mathrm{An}^{-\cdot}$$

$$\mathrm{E} + \mathrm{TEA}^{+\cdot} \longrightarrow \mathrm{Tw}^{+\cdot} + \mathrm{TEA}$$

$$\mathrm{E} + \mathrm{Tw}^{+\cdot} \longrightarrow \mathrm{Tw}^{+\cdot} + \mathrm{Z}$$

$$\mathrm{An}^{-\cdot} + \mathrm{Tw}^{+\cdot} \longrightarrow \mathrm{E} + \mathrm{An}$$



The high conversion eliminates the need of product purification.

---

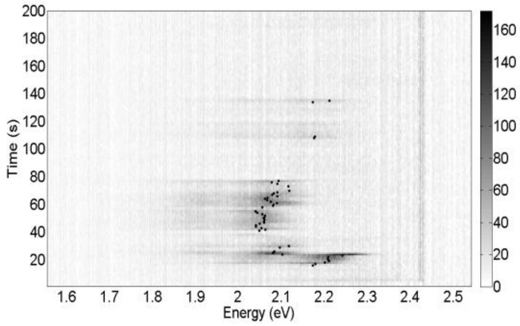
[1] M.J.Calverley. *Tetrahedron*. **43** (1987) 4609-4619

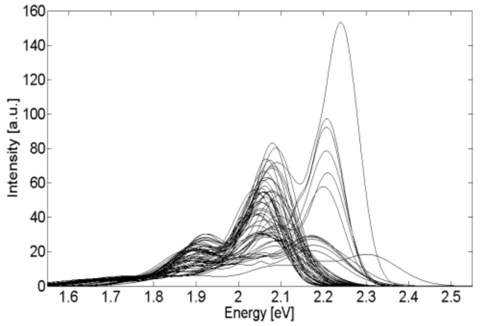
Acknowledgements. PFA is a member of CONICET. We thank Delta Biotech (Argentina) for HPLC analysis and for supplying (5-E-α calcidol).

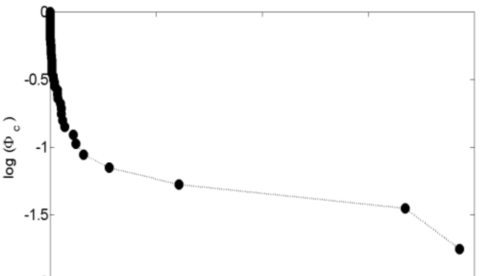
Cage effect on nanometer scale poly (n-alkyl) methacrylates films studied by Nile Red single molecule fluorescence spectroscopy

<u>Beatriz Araoz</u>[1], **Daniela Täuber**[2], **Christian von Borczyskowski**[2] **and Pedro F. Aramendia**[1]
[1]INQUIMAE y DQIAyQF. FCEN. UBA. Pab 2. Ciudad Universitaria. C1428EHA. Buenos Aires. E-mail: beatriz@qi.fcen.uba.ar; [2] Optical Spectroscopy und Molecular Physics Group, Chemnitz University of Technology, Faculty of Natural Sciences, Institute of Physics, TU-Chemnitz,Chemnitz, Germany

One of the most important properties of glassy polymers is the “glass transition temperature”, T_g. Several studies showed that T_g is influenced by confinement effect[1-2]. Poly n-alkyl methacrylate films of thickness below 100 nm show changes in T_g up to 20 ºC compared to bulk films. This result might have an impact on systems like Oleds where thin films are employed. For these reasons, we are interested on monitoring local cage changes near a fluorescent probe (Nile Red, NR) in poly (n-alkyl) methacrylates (n-butyl, PBMA, n-propyl, PPMA, and methyl, PMMA) films of nanometer scale. Studies were performed by single molecule fluorescence spectroscopy as a function of temperature and film thickness







Three types of NR emission spectra with different emission maximum were found in all the polymers (middle figure). Analysis of time traces of spectral fluctuations for every molecule was performed by using the energy difference between successive emission spectra (ΔE). We observe large jumps and small fluctuations of spectrum maximum position (upper and middle figures).

Statistical analysis was performed using the *complementary cumulative distribution function* of the energy difference ($\Phi_c(\Delta E)$), which gives the probability of observing a spectral change with absolute energy greater than a given value (lower figure). The analysis allows the estimation of transition probability and amplitude of the spectral changes. In PBMA films, both of them increase with temperature and are always greater in 200 nm films than in 25 nm ones.

This can be related to a decrease of NR local environments dynamics with film thickness (higher rigidity of 25 nm films).

(1) Priestley, R. D.; Mundra, M. K.; Barnett, N. J.; Broadbelt, L. J.; Torkelson, J. M. *Australian Journal of Chemistry* **2007**, *60*, 765.
(2) Ellison, C. J.; Torkelson, J. M. *Nat Mater* **2003**, *2*, 695.

Effect of solvent properties on the yield of major products in the photolysis of 1-Nitropyrene

Rafael Arce, Zulma García-Berríos
University of Puerto Rico – Río Piedras Campus, San Juan, PR

1-Nitropyrene (1-NO_2Py), a well known mutagenic and highly carcinogenic polycyclic aromatic hydrocarbon (PAH), is the most abundant nitrated PAH (nitro-PAH) emitted through different combustion processes. Its transformations in the atmosphere are still debated, and a possible environmental fate for 1-NO_2Py is through its photodecomposition on the atmospheric aerosols. This work describes studies on the photochemistry of particle-associated 1-NO_2Py in a chemical model system consisting of an organic solvent and known organic constituent of diesel exhaust particles and wood smoke particles. Photodestruction quantum yields of (0.5 – 1.7) x 10^{-3} were measured suggesting an inefficient photoreactivity of 1-NO_2Py compared to the other nitroaromatics (10^{-2}). The yield is influenced by the properties of the solvent (nonpolar, polar, polar aprotic) and the viscosity. Three major products have been identified: 1-OHpyrene, 1-OH-2-NO_2pyrene and 1-nitrosopyrene, whose yields are also affected by the properties of the solvents. In toluene or benzene, the 1-OHPy yield is null while 1-OH-2NO_2Py is the only product observed, in CCl_4 only 1-OH-2NO_2Py and diones are found, while in polar non protic acetonitrile the yield of 1-OH-2NO_2Py is four times higher than the yield of 1-OH-2NO_2Py. In alcohols the yield of 1-OHPy is about ten times higher than the yield of 1-OH-2NO_2Py, and a noticeable yield of 1-nitrosoPy is observed. The effects of additives, such as O_2 and phenols, on the yields of these products have also been studied. The results will be discussed in terms of the participation of postulated reaction intermediates and excited states in the photodestruction mechanism of nitroaromatics.

The financial support by NIH SCoRE (grant 5S C1ES17352-2) is gratefully acknowledged.

Synthesis, characterization and photophysical properties of silica nanoparticles modified with cinnamic alcohol.

Juliana Scotto[1,2]; Valeria B. Arce[1,2]; Mónica C. Gonzalez.[1], Patricia E. Allegretti[2] and Daniel O. Mártire[3]

[1] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, (1900) La Plata, Argentina.*

[2] *LADECOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina.*

Introduction

The surface of silica carries silanol groups [1], ≡Si-OH, which can be chemically modified to produce a covalently bonded organic layer which affects the chemical and physical properties of the silica [2].

We here prepared fumed silica nanoparticles modified with cinnamic alcohol through the esterification reaction of the surface silanol groups. The fluorescence emission spectra of suspensions of the particles were compared to those of solutions of cinnamic alcohol in different solvents.

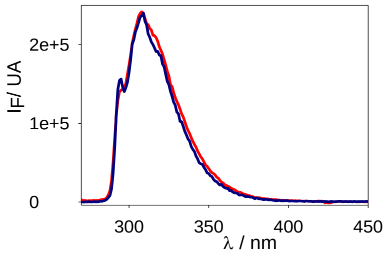
Experimental

To a suspension of silica in o-xylene, cinnamic alcohol was added. A continuous solid-liquid extractor was mounted on the reaction flask, and the mixture was refluxed. The heating rate was carefully regulated to obtain a continuous and stable flow of o-xylene through the extractor. After refluxing for 24 h was filtered through an HPLC filtration device and washed with ethyl acetate. The resulting gel was dried at 0.1 Torr. A white powder was obtained.

The obtained nanoparticles were characterized by FTIR spectra of the solid material and UV-visible absorption spectra of aqueous suspensions. The specific surface area (SSA) was measured from nitrogen adsorption isotherms (BET method).

Results

The emission spectrum of cinnamic alcohol in water has a component in the region of longer wavelengths which is absent in other solvents. The dependence of the emission spectra with the polarity of the solvent can be an indication of the existence of states of the type locally excited (LE) and internal charge transfer (ICT) [3]. Stabilization of the ICT in water would result in a reduction of the shoulder at 294 nm. The figure shows the emission spectrum of cinnamic alcohol in water (red line) and ethanol (blue line).



References

[1] Zhuralev, L.T. *Colloids Surfaces A: Physicochem. Eng. Aspects.*, **173** (2000) 1–38.

[2] Vansant, E.F., Van Der Voort, P., Vrancken, K.C. *Elsevier Science*, **3** (1995) 560.

[3] Lakowicz, J. R. Principles of Fluorescence Spectroscopy. 3 Ed.; Springer Science+Business Media: New York, **2006**.

Atmospheric Chemistry of 2-Ethyl Hexanal: Photochemistry and Oxidation in presence of NO_2

Juan Carlos Fraire, Fabio Ernesto Malanca* and Gustavo Alejandro Argüello
INFIQC (CONICET) – Departamento de Fisicoquímica – Facultad de Ciencias Químicas – Universidad Nacional de Córdoba. e-mail: fmalanca@fcq.unc.edu.ar

Aldehydes are important atmospheric constituents as they are emitted by a variety of sources (natural and anthropogenic). They arise from incomplete fossil fuel combustion, are emitted by vegetation and are produced during biomass burning as well as atmospheric oxidation of volatile organic compounds (VOCs). They are important precursors of radicals and peroxyacyl nitrates ($RC(O)OONO_2$)[1]. The atmospheric degradation of branched-chain aldehydes is controlled by photolysis and by reaction with OH radicals. [2,3] .

In this work we present a kinetic and photochemical study of 2-ethyl hexanal (2-Ethal, $C_4H_9CH(C_2H_5)C(O)H$). it is a volatile liquid used as solvent [4] and the main product of the atmospheric degradation of 2-ethyl hexanol (which is used in the manufacture of plastics, as an additive for lubricants, surfactants, etc.) [5-6]. Previous studies of the oxidation of this aldehyde proposes it as a new reagent to obtain 2-ethyl hexanoic acid [7-8]. According to these industrial scale use, an increase of it concentration in the atmosphere is expected, and therefore it is important to know its atmospheric behavior.

The rate constant (k) for reaction of 2-Ethal with Cl atoms was determined through a relative rate method with two reference compounds (i-pentane and cyclohexane). The mean value obtained ($k = (2.74 \pm 0.73) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) is in agreement with those expected for other long chain aldehydes. The oxidation mechanism in the presence of NO_2 was determined by using FTIR spectroscopy for the product analysis. The acyl radical forming channel was the most important in the oxidation mechanism leading to the formation of CO_2, CO, peroxyacetyl, peroxypropionyl, and ethyl nitrate. The mechanism proposed involves a series of aldehydes: formaldehyde, acetaldehyde and propyonaldehyde, which react to form the nitrates and peroxynitrates.

In order to determine the quantum yields of the molecule, the UV absorption cross section was recorded previously over the range 200-350 nm at 298 K. The 254 nm photolysis mechanism in 700 torr of O_2 was determined through FTIR analysis of the products. Two primary photodissociation channels occur: the formation of radicals and the dissociation in closed shell molecules. The total quantum yields ($\phi = 0.51 \pm 0.09$) agrees with those reported in bibliography for similar non-linear carbonated chain aldehydes. The formation of CO, heptane, 3-heptanol and 3-heptanone, as products of reactions are in accordance with the proposed mechanism.

References:

[1] Atkinson, R.; *J. Phys. Chem. Ref. Data, Monograph No. 2* (1994) 1.
[2] Thevenet, R.; Mellouki, A.; Le Bras, G.; *Int. J. Chem. Kinet.* 32 (2000) 676.
[3] Mellouki, A.; Le Bras, G.; Sidebottom, H.; *Chem. Rev.*; 103 (2003) 5077.
[4] Lehtinen, C.; Brunow, G.; *Org. Proc. Res. & Develop.* 3 (1999) 101.
[5] Edwards, R.D.; Jurvelin, J.; Koistinen, K.; Saarela, K.; Jantunen, M.; *Atmos. Environ.* 35 (2001) 4829.
[6] Nalli, S.; Horn, O.J.; Grochowalski, A.R.; Cooper, D.G.; Nicell, J.A.; *Environ. Pollut.* 140 (2006) 181.
[7] Gliński, M.; Kijeński, J.; *React. Kinet. Catal. Lett*. 55 (1195) 311.
[8] Gliński, M.; Kijeński, J.; *React. Kinet. Catal. Lett*. 55 (1195) 305.

Photophysics and Phase Transitions in *Poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-{2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene}] (PFO-MEHPPV)* Thin Films using Fluorescence Techniques.

Raquel A. Domingues, Bruna M. A. Bonon, Teresa D. Z. Atvars
Institute of Chemistry, Universidade Estadual de Campinas – UNICAMP, P.O. Box 6154, Campinas, 13084-971, SP, Brazil, e-mail: tatvars@iqm.unicamp.br

Conjugated polymers are used as thin active layers films in polymer light emitting diodes and photovoltaic devices. The morphology of these active layers is strongly dependent on the deposition process which also plays an important role in the device performance. In addition, even when the deposition processes were performed under the same conditions, thinner films may have different properties compared to the bulk. For example, properties such as glass transition temperature (T_g), diffusion coefficients and mobility of charge carriers in thin or ultrathin polymer films are seen to deviate from bulk values. Moreover, temperature is an important parameter that influences all the mobility processes in a polymer matrix. Thus, the knowledge of the thermal processes in thin films is relevant for the understanding of the device performance. Several studies using luminescence spectroscopy of thin films of vinylic and acrylic polymers and copolymers demonstrated that glass transition temperatures of thin films, supported or not on substrates, are different of that in thicker films[1]. Luminescence techniques are particularly useful because the sample preparation and instrument manipulation are relatively easy.

In this work we studied the role of the thickness (from 50 to 800 nm) on the phase transition and relaxation processes of the poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-*alt-co*-{2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene}] (PFO-MEH-PPV) using steady-state fluorescence spectroscopy. In a previous work[2] we showed that the packing model for the structure of thicker films was: stacked planes of the phenyl rings are separated by $\sim$4.5 Å and laterally spaced by $\sim$16 Å. In thicker films, polymer relaxation processes were followed the evolution of these distances as a function of temperature by WAXS, dynamical mechanical thermal analysis, fluorescence and solid-state nuclear magnetic resonance showing: $T_\beta = 213$ K (side-chain motion, with a small increase in the lateral spacing and in the stacking distance of the phenyl rings in the aggregated structures). Here, using fluorescence spectroscopy (other techniques are very complicated when using thin films) we verified that the temperature transitions decreased with decreasing film thickness. We also observed changes in the emission spectra for thinner films of different thicknesses with the presence of an isoemissive point which suggests that changes between species are occurring.

Acknowledge: Authors thank FAPESP, CNPq and INEO/FAPESP/CNPq for financial supports and fellowships.

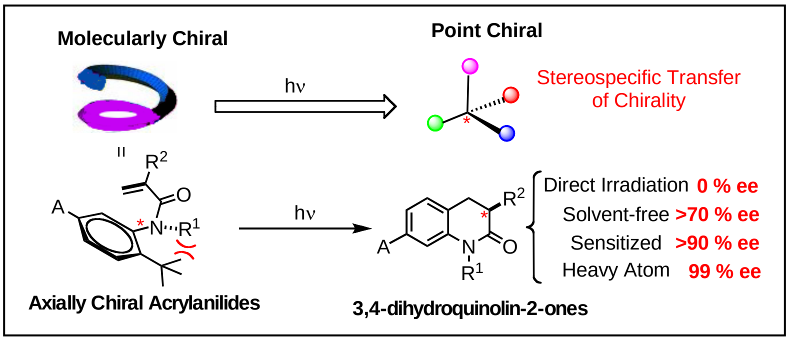
[1] S. Kim, M. K. Mundra, C. B. Roth, J. M. Torkelson. Macromolecules 43, 5158 (2010).

[2] G. C. Faria, T. S. Plivelic, R. F. Cossiello, A. A. Souza, T. D. Z. Atvars, I. L. Torriani, and E. R. deAzevedo. J. Phys. Chem. B 113, 11403–11413 (2009).

Enantiospecific Chiral Transfer: Role of Reaction Media and Reactive Spin States in the 6π-Photocyclization of Axially Chiral α-Substituted Acrylanilides

Anoklase J.-L. Ayitou and J. Sivaguru*
Department of Chemistry and Biochemistry, North Dakota State University
Fargo, ND 58108 - 6090 USA.

Asymmetric photochemical reactions have not enjoyed the same level of success as their thermal counterparts. This is in part due to the short lifetime in the excited state and/or the lack of energetic bias for the discriminatory formation of enantiopure products. In this regards, predisposing photo – candidates with stereospecific geometry will undoubtedly lead to prochiral intermediate(s) in the transition/excited state that will produce chirally enriched photoproduct(s). This poster will present our ongoing investigations of employing molecularly chiral chromophores for photochemical transformations. As a model system we have investigated the 6π-photocyclization of axially chiral α-substituted acrylanilides leading to enantiopure 3,4-dihydroquinolin-2-ones. The enantioselectivity (with up to 99 % *ee*) in the photoproduct depends on the reactive spin state and the type of medium employed for the photochemical transformation. Direct irradiation via a singlet excited state (S_1) produces racemic mixture of the photoproduct, while the sensitized irradiation *via* triplet excited state (T_1) leads to *ee* values of >90%. We were also successful in demonstrating heavy atom effect in the stereospecific process in solution. High enantioselectivities *via* direct irradiation were observed for solid-state (solvent-free) reactivity. This poster presentation will highlight the rational of spin dependence, the influence of heavy atom and the role of the reaction media on the enantioselectivity during 6π-photocyclization of axially chiral α-substituted acrylanilides.



Some Relevant References:

Ayitou, A. J.-L.; J. Sivaguru. *J. Am. Chem. Soc.* **2009**, *131*, 5036.
Ayitou, A. J.-L.; Ugrinov, A.; J. Sivaguru. *Photochem. Photobiol. Sci.* **2009**, *8*, 751.
Ayitou, A. J.-L.; J. Sivaguru. *Chem. Commun.* **2011**, *47*, 2568.
Ayitou, A. J.-L.; Vallavoju, N.; Ugrinov, A.; J. Sivaguru.**2011**, *in press,* DOI:10.1039/C1PP05057E.

Generation and suppression of singlet oxygen in hairs by photosensitization of melanin

Orlando Chiarelli-Neto, Christiane Pavani, Alan da Silva Ferreira, Divinomar Severino, Maurício S. Baptista
Departamento de Bioquímica, Instituto de Química, Universidade de São Paulo, Brasil

We have studied spectroscopic properties of hairs (white, blond, red, brown and black) under illumination with visible light, giving special emphasis to the photo-induced generation of singlet oxygen ($^1O_2$). Hairs were excited by 532nm light and $^1O_2$ spectra were obtained by measuring emission from 1200 to 1300 nm. All hair shafts presented $^1O_2$ emission whose intensity varied inversely with their colors, i.e. black and brown hairs presented similar intensities and the others (white, blond and red) generated significantly larger amounts of $^1O_2$. $^1O_2$ lifetime was also measured and shown to vary with hair type being 5 times shorter in black hair compared with blond hair, indicating the role of melanin as $^1O_2$ suppressor. Lifetimes ranged from tenths of nanosecond to few microseconds, which are much shorter than the lifetime expected for $^1O_2$ in the solvents in which hair shafts were suspended, indicating that $^1O_2$ is generated and suppressed inside the hair structure. The higher amount of $^1O_2$ generated in blond hair and its longer lifetime is compatible with the stronger damage that light exposition causes in blond hairs. Pure melanin samples were also shown to produce $^1O_2$, indicating that this biopolymer is responsible for the generation and suppression of $^1O_2$. A model for the production and suppression of $^1O_2$ in hairs is proposed (Figure 1). Our results prove the role of $^1O_2$ in the mechanism of hair damage. We also have opened a new window of investigations concerning the effect of over-exposition of biological surfaces to visible light. This understanding is important to develop new strategies to protect skin and hair from the effects of over exposition to the sun.

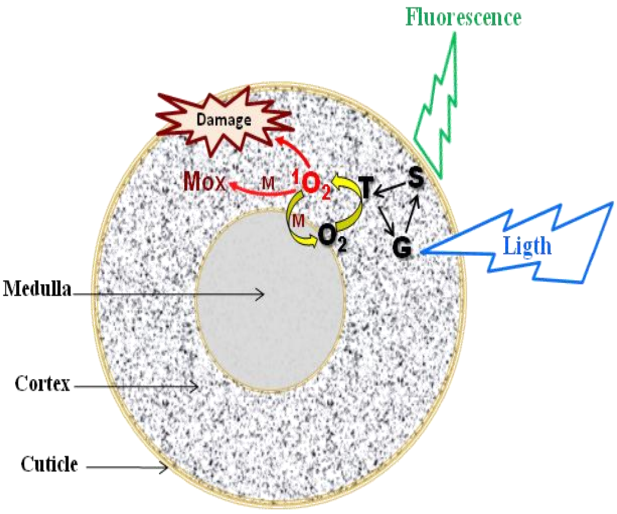


Figure 1: Photophysical and photochemical processes in a hair shaft under irradiation showing production of singlet oxygen ($^1O_2$) by photosensitization after irradiation with visible light. The process starts mainly in the region where melanin is present (cortex). G is ground state of Melanin; S is its singlet state; T is its triplet state. G absorbs light forming S that converts to T through intersystem crossing and T reacts with oxygen forming $^1O_2$. $^1O_2$ can be suppressed by three main processes: physical quenching (mainly my melanin) returning heat and molecular oxygen, chemical quenching by melanin forming oxidized melanin (M_{ox}) or by reacting with other aminoacid residues like cysteine of keratin, causing damage in the hair structure. Cross section of the hair shows cuticle, cortex and medulla, which are out of scale.

A TDDFT Basis Set and Functional Assessment for the Calculation of Electronic Excitation Energies of Fluorenes

Cristina A. Barboza[1], Pedro A. M. Vazquez[2], Desmond Mac-Leod Carey[1] and Ramiro Arratia-Perez[1]

[1] *Departamento de Ciencias Químicas, Universidad Andres Bello, Relativistic Molecular Physics (ReMoPh) group, Republica 275, Santiago, Chile*

[2] *Instituto de Química – Caixa Postal nº 6154 Universidade Estadual de Campinas – UNICAMP 13083-970, Campinas, SP, Brasil*

Fluorene containing molecules represent an important class of aromatic systems that have received considerable attention due to their unique photophysical properties[1,2]. They are used as as biosensors, light-emitting diodes, solar cells, and as building blocks for the design of p-type materials for photovoltaic applications[3].Recent gas phase UV spectra measurements have made a complete assignment of all observed bands in the 100-350nm region. TDDFT calculations failed to reproduce this assignment,so the aim of this work is to compute the five low lying optically active electronic states of fluorene using Linear Response/Coupled Cluster Singles and Doubles (LR/CCSD) and Sadlej-pVTZ basis set and use these results to assess how a set of standard functional/basis sets performs in reproducing the higher level model. A C_{2v} HF/cc-pVDZ optimized geometry was used in all calculations. The Dalton-2.0 program was used to compute the excitation energies with the B3LYP, CAM-B3LYP, PBE0 and LB94 functionals, while the the nwchem-6.0 package was used to compute the electronic transitions with the Casida-Salahub corrections (CS00) for the B3LYP functional. The performance of the following basis sets with was assessed: 6-31G**, 6-31++G**, 6-311G**,6-311++G**, cc-pVDZ, aug-cc-pVDZ, Sadlej-pVTZ and p-SBKJC. Our results show that the LR/CCSD methodology always correctly predicts the experimental assignment and qualitatively reproduces the band intensities but none of the DFT methods was able to predict the correct 2a1 and 2ab2 energies. This may be due the contribution of double excitations to these transitions, as diagnosed by CCSD analysis, absent in an singles method as TDDFT. the B3LYP/CS00 and PBE0 show the best agreement for the first excitations while CAMB3LYP performs better, on average, in the interval investigated.

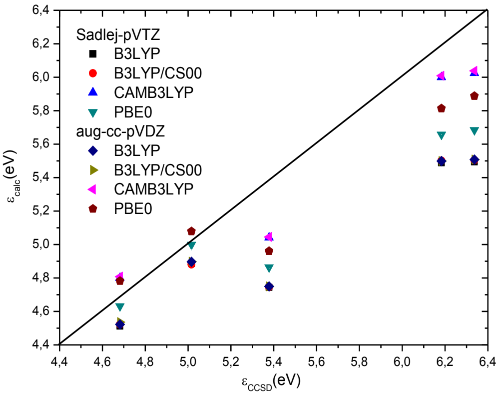


Figure 1. TDDFT performance of the functional with respect to CCSD/Sadlej-pVTZ.

References: **(1)** Cheng, Y.-J. Yang, S.-H.; Hsu, C.-S., *Chem. Rev.* **2009** 109, 58868. (**2**) Nguyen, D. D.; Trunk, J.; Nakhimovski, L.; Spanget-Larsen, J., *J. Mol. Spectr.* **2010** 264, 19. (**3)** Zhou, Q.; Hou, Q.; Zheng, L.; Deng, X.; Yu, G.; Cao, Y., *Appl. Phys. Lett.* **2004** 84, 1653.

Acknowledgments: The authors thanks the financial support of FONDECYT Grants 1100283 and 1110758[1], PROJECT MILLENNIUM No. P07-006–F[1] and TWAS/CNPq, Process nº 190063/2009-2[2].

Theoretical Study of the Effect of the Substitution of Donor and Acceptor Groups Over the Electronic and Structural Properties of the 9,9'-dimethylfluorene Dimer

Cristina A. Barboza, Desmond Mac-Leod Carey and Ramiro Arratia-Perez
Departamento de Ciencias Químicas, Universidad Andres Bello, Relativistic Molecular Physics (ReMoPh) group, Republica 275, Santiago, Chile

Modulation of physical and chemical properties of molecules by the substitution of electron donor and acceptor groups has attracted considerable attention in the context of material science, with particular interest on the study of conjugated polymers as fluorene derivatives[1]. Fluorene-based oligomers and polymers have been extensively studied for applications as biosensors, light-emitting diodes and solar cells due their emission at wavelength spanning the entire visible spectrum and high fluorescence efficiency[3].

The aim of this work is to study the effects exerted by the substitution of the 3-position on the structural and electronic properties of 9,9'-dimethylfluorene dimer (Fig. 1). The calculation of excitation energies, ground state potential curves and Walsh diagrams at density functional theory (DFT) level are presented. The chosen density functional and basis set were B3LYP/6-31+G**. Ground state potential energy curves were obtained at the same level, calculated for fixed angles using the relaxed scan from the interval 0 to 180° with a 10° step size. Characterization of electronic transitions where then performed by applying time-dependent DFT method on their corresponding optimized ground state structures.

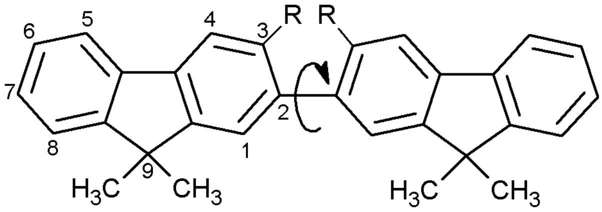


Figure 1. Molecular structure of studied fluorene-based dimers where R = H, $-CH_3$,$-NH_2$, $-OH$, $-Cl$, $-F$, $-NO_2$ and $-COOH$.

The calculated electronic transitions for the non-substituted dimer are in good agreement to the experimental data, corresponding to $\pi \rightarrow \pi^*$ type excitations, with $\lambda_{\text{máx}}$ being shifted by substitution from 0.03 to 0.57 eV for $–OH$ and $–CH_3$, respectively. Walsh diagrams indicate that the effect of the substitution over the HOMO energies of the non-substituted dimer is more pronunciated for $-NH_2$ and $-Cl$. All the substituents disturb severely the ground state potential energy profiles. Substitution of the fluorene backbone with donor or acceptor groups changes the energies of the frontier molecular orbitals, allowing a significant modulation of the molecular electronic properties of these systems.

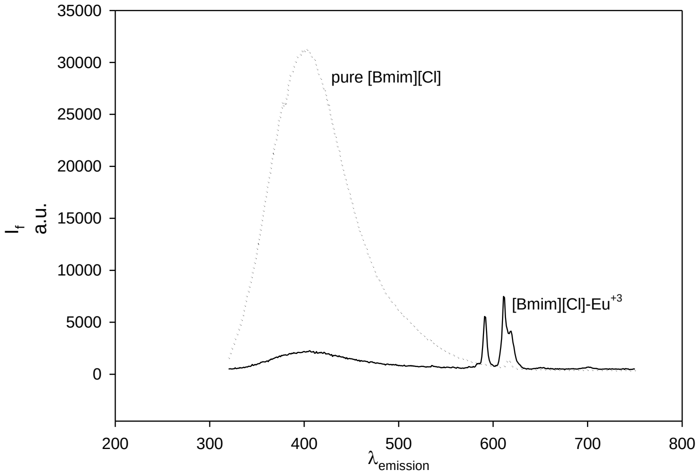
References:
1. Bredás, J. L.; Heeger, A. J., *Chem. Phys. Lett.* **1994**, 5-6 507-512
2. Gong, Z.; Lagowski, J. B., J. Mol. Struc.: THEOCHEM **2008**, 866, 27-33.
3. Zhou, Q.; Hou, Q.; Zheng, L.; Deng, X.; Yu, G.; Cao, Y., *Appl. Phys. Lett.* **2004**, 84, 1653-1655.

Acknowledgments:
The authors thank the financial support of FONDECYT Grants 1100283 and 1110758, and PROJECT MILLENNIUM No. P07-006–F

Effect of the Eu^{+3} on the Ionic Liquid 1-butyl-3-methylimidazolium Chloride luminescence

Beatriz Barja [1,2] **and Karin Gutkowski** [2,3]
[1] *Departamento de Química Inorgánica, Analítica y Química Física, FCEN, Universidad de Buenos Aires, 1428, Buenos Aires, Argentina.*
[2] *Member of Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET.*
[3] *CNEA- CAC- Gerencia de Química, Av. Gral. Paz 1499, 1650 San Martín, Pcia. de Buenos Aires, Argentina.*

Ionic liquids, formed by an organic cation and an anion (organic or inorganic) are a new generation of solvents, with negligible vapor pressure and high chemical stability, which is called to replace organic volatile solvents. Specifically, the substituted methylimidazolium- like ionic liquids present photoluminescence together with a red edge effect (~ λ_{exc}=270-450 nm). Lanthanides, present very narrow bands and long lifetimes of the excited states. Lanthanides´ weak absorption (low molar absorption coefficient) results in a low intensity of their photoluminescence. That is why; the photochemistry of the lanthanides is usually accompanied by the addition of a antenna specie in the system. Some studies on the solvation of the lanthanide immersed in an IL, show that actually, the specie solvated is the $(LnCl_n)^{3-n}$.
We study specifically the photoluminescent behavior of the system 1-butyl-3-methylimidazolium Chloride-Eu^{+3}, [Bmim][Cl]-Eu, along the whole excitation/emission spectra of the system. Steady state and time resolved fluorescence measurements were performed for different Eu^{+3} concentrations in the ionic liquid. (one of the spectrum is shown in the figure as an example).



The results show a very high quenching by the Eu^{+3} on the IL fluorescence at high excitation energies while at low energies the predominant effect is the antenna role of [Bmim][Cl] that increases the Eu^{+3} fluorescence intensity value, I_f^{Eu}, in comparison to the I_f^{Eu} when the Europium is directly excited.

The observations are discussed in terms of the energy transfer efficiency calculated as $(A^*_{IL}-A_{IL})/ A^*_{IL}$ in the IL emission range and as $(A^{466}_{Eu}-A_{Eu})/ A^{466}_{Eu}$, with A_{IL} and A_{Eu}, being the emission area in the IL emission range and in the Eu^{+3} emission range respectively; and, A^*_{IL}, the area for the pure IL emission; A^{466}_{Eu}, the Eu^{+3} emission are when it is excited at 466nm (direct excitation).

Luminescent materials based on Ceria, gadolinium and europium oxides

Cecilia Sorbello, Beatriz C. Barja and Matías Jobbagy
INQUIMAE / DQIAyQF. Facultad de Ciencias Exactas y Naturales. UBA.
Ciudad Universitaria, Pab. 2, Piso 1, C1428EHA Ciudad de Buenos Aires. Argentina

Lanthanides are widely used to develop solid luminescent materials (phosphors) with technological applications in the field of light conversion: luminescent lamps, diodes, and optical fibers for telecommunications.[1] These ions display a well-defined luminescence characterized by very narrow (a few nm) and highly structured emission bands with lifetimes in the millisecond timescale. Their almost monochromatic emission makes them especially useful for optical purposes.

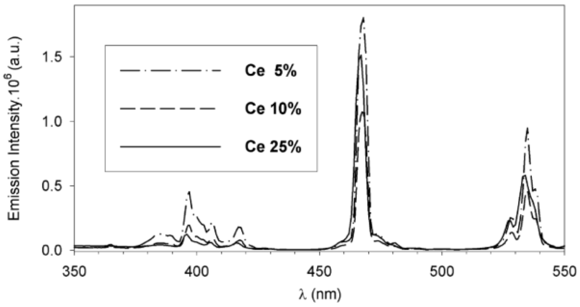
In this work luminescent microparticles (average 100 nm) were synthesized with the homogeneous phase precipitation method through the thermal hydrolysis of urea with a high control of morphology and size. The control of these characteristics is particularly useful to develop luminescent solid materials to fabricate luminescent screens.

The structural and emission properties of a family of oxides (Ce_{1-x} Gd_x) with a fixed amount of Eu(III) were studied for x = 0, 0,05, 0,10, 0,25, 0,50, 0,75 and 1,0.

The amorphous precursors obtained by controlled heating at 90°C were finally filtered, dried and calcinated at 1000°C in air.

The techniques used to characterize these particles were stationary emission spectroscopy (at room temperature and 77 K), powder X-Ray diffraction and high resolution scanning electron microscopy (HRSEM) coupled with dispersive energy X-Ray diffraction (EDS).

The band assignment for the intra 4f-f transitions of Eu(III) and Gd(III) as well as for the charge transfer transitions of Eu(III) and Ce(IV) was performed and the energy transfer mechanisms were analyzed.



The graph shows the excitation spectra of three Ce(IV)/Gd(III) oxides with 5% Eu(III) for λ_{em}= 612 nm. The bands correspond to the $^7F_0 \rightarrow {}^5D_J$ (J= 0,1,2,3,4) and $^7F_0 \rightarrow {}^5L_6$ Eu(III) transitions. From the graph it can be observed that an increase in the Ce(IV) does not yield the corresponding proportional increase in the intensities of the Eu(III) bands. This result together with the change in the profiles of the bands indicate that the Eu(III) sense changes in the environment in which it is located.

Considering that the Gd_2O_3 oxide has a c-type structure (C_2 and S_6 sites) and that CeO_2 has an octahedral fluorite structure (O_h), the analysis of these bands for different x values can help elucidating the actual structure of the binary system as a complimentary alternative to the X-Ray technique.

1 W. M. Yen, Sh. Shionoya y Hajime Yamamoto. Phosphor Handbook, CRC Press, 2007

Synthesis, Characterization and Use of Porphyrin and Phthalocyanine Chromophoresin Solar Energy Conversion

Jesse J. Bergkamp[1], **Benjamin D. Sherman**[1], **Matthieu Koepf**[1], **Smitha Pilla**[1], **Gerdenis Kodis**[1], **Tom Moore**[1], **Devens Gust**[1], **and Ana Moore**[1]
1) Department of Chemistry and Biochemistry, Arizona State University, Tempe Arizona 85287-1604

Photosynthesis is one of the most important processes in nature as it has provided all of the oxygen on earth, as well as the fossil fuels we use today for our energy needs. The process of converting incident solar energy into chemical potential energy via photo-induced electron transfer is what we aim to mimic with our synthetic constructs. Herein we are presenting three projects that pertain to photo-induced stepwise electron transfer, water oxidation, and hydrogen production. Each of these three projects uses porphyrin and/or phthalocyaninechromophores for light energy capture. For the electron transfer studies, phosphorus porphyrins are being investigated because of their strong electron accepting capabilities. In order to gain insight into electron transfer in photosystem II (PSII), we are studying the chemistry of linking phosphorus porphyrins to a porphyrin bearing a phenol-benzimidazole, a tyrosine-histidine model. The design of this triad mimics the donorside of PSII and should give insight into the proton coupled electron transfer (PCET) processes that take place during photosynthesis. For the investigation into water oxidation, a high potential5,15-bis(pyridyl)-10-benzylmalonate-20-(phenylphosphonate) porphyrin has been synthesized and preliminary experiments have been attempted for attachment to TiO_2. The malonate functional group has been shown to preferentially bind to IrO_2 and the phosphonate to TiO_2[1] for use in a photoelectrochemical cell (the IrO_2 acts as a catalyst for water oxidation). Silicon octabutoxy-phthalocyanines are being used in the investigation of photoelectrochemical cells which mimic photosystem I (PSI) and the production of hydrogen. Currently, the chemistry of synthesizing an axial phenyl-phosphonatephthalocyanine is under way. The phosphonate group will be usedas the attachment site to semiconductors with highly negative conduction bands, which is needed to carry out the reduction of H^+ to H_2 effectively.

1) Hoertz, P.G.; Yeong-Il, K.; Youngblood, J.W.; Mallouk, T.E. *J. Phys. Chem. B***2007**, 111, 6845-6856

Reduction of mercury (II) by carbon dioxide radical, generated from the interaction of formate with the triplets states of 1,4-naphthoquinone.

Andrea M. Berkovic[1,2], **Mónica C. Gonzalez**[1], **Reinaldo Pis Diez**[2], **Sonia G. Bertolotti**[3], **and Daniel O. Mártire**[1]
[1] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. C. 16, Suc. 4, (1900) La Plata, Argentina. E-mail: a_berkovic@yahoo.com*
[2] *Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Facultad de Ciencias Exactas, Universidad Nacional de la Plata, C.C. 962, B1900 AVV La Plata, Argentina.*
[3] *Departamento de Química, Laboratorio de Fotoquímica de la Universidad Nacional de Río Cuarto, (5800) Rio Cuarto, Argentina*

Abstract:
Mercury is one of the most important environmental contaminants that need more attention from policy makers, industry, and general public. This contaminant is toxic, persistent, and long-lived in the atmosphere. Coal combustion is believed to be the main source of mercury emissions to the atmosphere. Because of mercury cycles, it can be carried over long distances away from its initial source location. Mercury is mainly deposited into the aquatic environments through precipitation. Once in the aqueous phase, some biological processes transform mercury into organic compounds (methylated mercury compounds), which are extremely toxic and can be accumulated in fish, and can present significant risk for the human health. For these reasons it is necessary to develop methods of water treatment based on the elimination of mercury from waters.

In this work we investigated the photo-induced reduction of Hg (II), in aqueous solutions of $HgCl_2$ by the carbon dioxide radical anion, $CO_2^{\cdot-}$, which presents a suitable redox potential for the reduction of Hg (II) in solution (E^o= 0.85 V vs. NHE). The $CO_2^{\cdot-}$ radical anions were generated by photolysis of aqueous solutions of 1,4-naphthoquinone (NQ) in the presence of formate ion in excess [1]. As the $CO_2^{\cdot-}$ is a one-electron reducing agent, it transforms Hg (II) into Hg (I), which is insoluble in the presence of chloride ion. Thus, the method allows the elimination of mercury ions from the solutions.

The laser flash-photolysis technique with excitation at 355 nm was employed to investigate the reaction mechanism at room temperature. Due to the high absorbance of the solutions below 300 nm, the direct detection of the $CO_2^{\cdot-}$ was not possible. For this reason, methyl viologen (MV^{2+}) was used as a probe to detect the formation of $CO_2^{\cdot-}$. This radical is able to reduce the MV^{2+} to $MV^{\cdot+}$, a radical species that presents a characteristic absorption spectrum in the UV-Vis (λ_1^{max} = 390 nm and other λ_2^{max} = 600nm) [2], allowing therefore the indirect monitoring of the $CO_2^{\cdot-}$ radical.

References
[1] I. Loeff, S. Goldstein, A. Treinin and Henry Linschitz. *J. Phys. Chem., 95, 4423-4430 (1991)*
[2] T. N. Das, T. K. Ghanty, y H. Pal, *J. Phys. Chem.*, 107, 5998 (2003).

Singlet oxygen quenching by β -carotene in HeLa cells

Gabriela Bosio[1,2], **Thomas Bretenbach**[2] , **Frances H. Blaikie**[2], **Brian W. Pedersen**[2],
Daniel Mártire[1] **and Peter Ogilby**[2]
[1]Instituto de Investigaciones Teóricas y Aplicadas, Universidad Nacional de LA Plata, Argentina,[2] Center for Oxygen Microscopy and Imaging, Department of Chemistry, University of Aarhus, Denmark

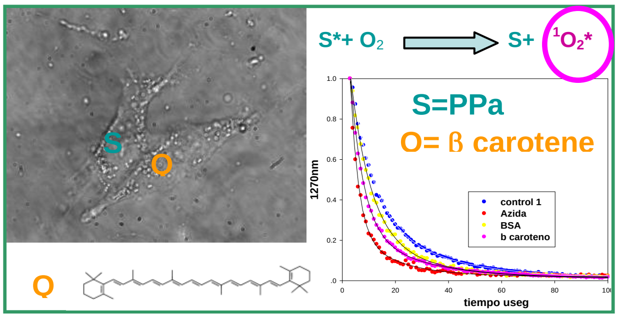
In this work we investigated the β-carotene quenching of singlet oxygen, $O_2(a^1\Delta_g)$, sensitized by different dyes with different subcellular localization.

Fluorescence and Resonance Raman Microscopy were used as non-invasive methods to investigate the subcellular localization of β–carotene in HeLa cells. To improve the fluorescence emission of the carotene, it was also synthesizeda carotene moiety covalently bonded to a fluorescein derivative.

Using a variety of different sensitizers, the $O_2(a^1\Delta_g)$ phosphorescence decay was monitored in cells suspensions, both in the absence and presence of β–carotene. The results were compared to those obtained with other singlet oxygen quenchers (bovine serum albumin (BSA), and sodium azide.

The ability of β-carotene to quench the $O_2(a^1\Delta_g)$ signal depended on the sensitizer used. For example when using a hydrophilic sensitizer, the hydrophobic β-carotene had little effect on the $O_2(a^1\Delta_g)$ signal whereas hydrophilic sodium azide had a large effect.

However, for sensitizers localized in thin hydrophobic membranes, β-carotene and sodium azide were both efficient quenchers of the $O_2(a^1\Delta_g)$ signal. These data are consistent with the notion that $O_2(a^1\Delta_g)$ formed in the bilayer can diffuse out into hydrophilic domains. Quenching of $O_2(a^1\Delta_g)$ by BSA, which is localized in the extracellular domain, indicates that $O_2(a^1\Delta_g)$ can also diffuse across the plasma membrane.

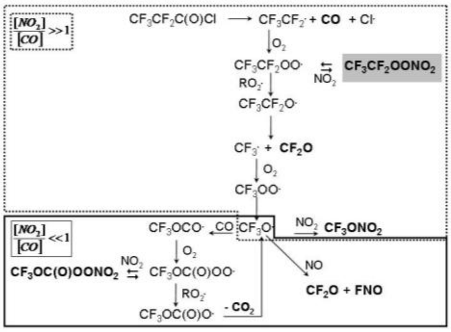


Synthesis and characterization of pentafluoroethyl peroxynitrate, $C_2F_5OONO_2$. Photooxidation of $C_2F_5C(O)Cl$ in the presence of NO_2

<u>Adriana G. Bossolasco</u>, Fabio E. Malanca* and Gustavo A. Argüello
INFIQC (CONICET) – Departamento de Fisicoquímica – Facultad de Ciencias Químicas – Universidad Nacional de Córdoba. e-mail: fmalanca@fcq.unc.edu.ar

Peroxynitrates ($ROONO_2$) are important species in the atmosphere because they act as reservoirs of NO_2 and $ROO^{\cdot}$ radicals. Their atmospheric thermal lifetimes (from hours to several days)[1] are sufficiently long to be transported from their sources to remote places or to the stratosphere[2]. Industrial compounds such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and hydrofluoroethers (HFEs) lead to the formation of fluorinated peroxynitrates, for example, trifluoromethyl (CF_3OONO_2), trifluoroacetyl ($CF_3C(O)OONO_2$), and trifluoromethoxycarbonyl ($CF_3OC(O)OONO_2$) peroxynitrates.[3,4]

In this work we present the photochemical synthesis and characterization of pentafluoroethyl peroxynitrate, $C_2F_5OONO_2$. The synthesis was carried out by photolysing $C_2F_5C(O)Cl$ at 254nm (that provides the C_2F_5 fragment)[5] in presence of NO_2 and O_2. To establish the correct experimental conditions for the synthesis, the mechanism of photooxidation of $C_2F_5C(O)Cl$ in the presence of NO_2 and O_2 was previously studied. Photolysis was run in a standard infrared glass cell, located in the optical path of a FTIR equipment to follow the temporal variation of reactant and products. The photolysis leads to the formation of $C_2F_5OONO_2$ (54%), CF_2O (63%), CF_3ONO_2 (12%) and CO as the main carbonated products, at short photolysis time. As time evolves, the CO concentrations increase in the system and NO_2 decrease, leading to the formation of CF_2O, CO_2 and $CF_3OC(O)OONO_2$. It can be seen a slow disappearance of $C_2F_5OONO_2$, which act as a reservoir of the NO_2 needed for the production of $CF_3OC(O)OONO_2$. A complete reaction mechanism explaining the formation of the products is presented in the Figure.



The synthesis of $C_2F_5OONO_2$ was carried out in a 5 L glass flask maintained at -20 ºC. The progress of its formation was followed every 30 min. through infrared spectroscopy and was stopped when NO_2 concentration decrease to one third of its initial concentration. After photolysis, the mixture was collected by slowly passing it through three traps kept at -186ºC, to remove the excess of O_2. $C_2F_5OONO_2$ was further purified by distillation.

The infrared spectrum and thermal stability of $C_2F_5OONO_2$ was determined. Absorption infrared cross-sections at the main peaks (2.54, 1.63, 4.8, 1.57, 2.2, 1.11 x 10^{-18} cm^2 $molecule^{-1}$ at 1764, 1304, 1244, 1188, 1085 and 790 cm^{-1} respectively) were measured. Kinetics parameters for its thermal decomposition between 279 and 290 K at total pressure of 9.0 and 200 mbar show that its thermal stability depends on the temperature as well as the total pressure, like in other peroxynitrates: (E_a = 84,2 and 96,5 kJ/mol, at 9 and 200 mbar respectively). Comparison with another peroxynitrates and atmospheric implications are also presented.

References

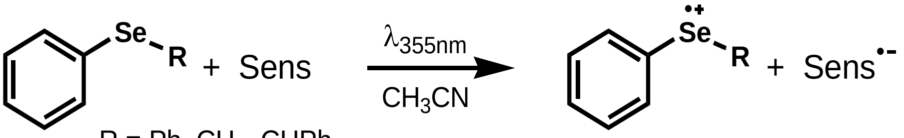
[1] Kirchner, F.; Mayer-Figge, A.; Zabel, F.; Becker, K.H. *Int. J. Chem. Kinet.* 31 (1999) 127.
[2] Ko, M.K.W.; Sze, N.D.; Rodriguez, J.M.; Weistenstein, D.K.; Heisey, C.W.; Wayne, R.P.; Biggs, P.; Canosa-Mas, C.E.; Sidebottom, H.W.; Treacy, J. *Geophys. Res. Lett.* 21 (1994) 101.
[3] Von Ahsen, S.; Garcia, P.; Willner, H.; Argüello, G. A. *Inorg. Chem.* 44 (2005) 5713.
[4] Mayer-Figge, A., Zabel, F., Becker, K.H., 1996. *J. Phys. Chem.* 100 (1996) 6587.
[5] Malanca, F.E., Burgos Paci, M. and Gustavo A. Argüello. *J. Photochem. Photobiol.* 6029 (2002)

Generation of Phenyl Alky and Diphenyl Selenide Radical Cations: A Laser Flash Photolysis Study

<u>Lydia M. Bouchet</u>, Alicia B. Peñéñory and Juan E. Argüello
INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba, Córdoba, Argentina, lbouchet@fcq.unc.edu.ar

Organic selenium compounds have been suggested to have antioxidant properties due to the rather low one-electron reduction potentials of the corresponding radical cations. Some mechanistic aspects and synthetic potentials of photoinduced electron transfer (PET) activation of organoselenium substrates have been explored by Pandey et al.[1] These interesting studies have been useful in initiating various synthetic reactions. However, direct evidence of the mediation of selenide radical cations or of other electrophilic selenium and carbocations species is further needed.

In the present communication the radical cations of PhSePh (**1**), PhSeMe (**2**) and PhSeCHPh$_2$ (**3**) have been produced by PET in acetonitrile solution, using dicyano naphthalene (DCN), *N*-methylquinolinium (NMQ$^+$) and 2,4,6-triphenyl thiapyrylium (STPP$^+$) cations, and Chloranil (Ch) as photosensitizers. The fluorescence of DCN and the low-lying triplet state of STPP$^+$ and Ch are quenched by selenides at diffusion rate constants, in agreement with the high exergonic value of those of ΔG_{ET} calculated by the Gibbs free energy equation. The nature of the PET step was confirmed by the observation of the semireduced form of the sensitizer, namely, DCN and Ch radical anions and the NMQ radical by the laser flash photolysis technique (eq 1).



(1)

R = Ph, CH$_3$, CHPh$_2$
Sens = DCN, NMQ$^+$, STPP$^+$, Ch

Thus the PhSeR radical cations were observed for the first time by transient absorption spectroscopy (Figure 1). PhSePh$^{\cdot+}$ presents three maximum absorption bands in agreement with pulsed radiolysis experiments.[2] The monomeric form of PhSeMe$^{\cdot+}$ and PhSeCHPh$_2$$^{\cdot+}$ shows a maximum at 500 nm; however, another band at 640 nm was observed for the former, attributed to a σ-dimmer between the selenide radical cation an a neutral molecule, similar to its periodic neighbor PhSeMe$^{\cdot+}$.[3] Cosensitizers such as toluene or biphenyl were necessary to avoid back-electron transfer for NMQ$^+$ and DCN, respectively. Finally, the life times of the selenide radical cations depend on the sensitizer employed and the concentration of molecular oxygen. Different reactions channels will be discussed in order to explain these observations.

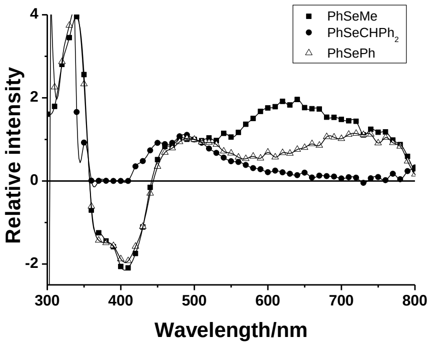


Figure 1: Transient absorption spectra for PhSeR (5mM) and STPP+ (0.06mM) observed at 0.25us after the laser excitation (■) PhSeMe, (●) PhSeCHPh2 and (△) PhSePh.

References
[1] Pandey, G.; Gadre, S. R. *Acc. Chem. Res*. **2004**, *37*, 201-201.
[2] Engman, L.; Lind, J.; Merényi, G. *J. Phys. Chem.* **1994**, *98*, 3174-3182.
[3] Yokoi, H.;Hatta, A.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12728-12733.

Glossary of Terms used in Photocatalysis and Radiation Catalysis (IUPAC Recommendations 2011)*

Silvia E. Braslavsky,[1] André M. Braun,[2] Alberto E. Cassano,[3] Alexei V. Emeline,[4] Marta I. Litter,[5] Leonardo Palmisano,[6] Valentin N. Parmon,[7] and Nick Serpone[8]

[1]Max-Plank-Institut für Bioanorganische Chemie (formerly für Strahlenchemie), Mülheim/Ruhr, Germany; [2]University of Karlsruhe, Germany; [3]Universidad Nacional del Litoral, Santa Fe, Argentina; [4]V.A. Fock Institute of Physics, St. Petersburg State University, St. Petersburg, Russia; [5]*National Atomic Energy Commission, Buenos Aires, Argentina;* [6]University of Palermo, Palermo, Italy; [7]Boreskov Institute of Catalysis, Novosibirsk, Russia; [8]Concordia University, Canada and University of Pavia, Italy

This glossary of terms covers phenomena considered under the very wide terms *photocatalysis* and *radiation catalysis*. A clear distinction is made between phenomena related to either photochemistry and photocatalysis or radiation chemistry and radiation catalysis. The term radiation is used here as embracing electromagnetic radiation of all wavelengths, but in general excluding fast moving particles. Consistent definitions are given of terms in the areas mentioned above, as well as definitions of the most important parameters used for the quantitative description of the phenomena. Terms related to the up-scaling of photocatalytic processes for industrial applications have been included. This Glossary should be used together with the *Glossary of Terms used in Photochemistry*, 3rd version, IUPAC Recommendations 2006: (http://www.iupac.org/publications/pac/79/3/0293/) as well as with the IUPAC Compendium of Chemical Terminology, 2nd Edition (the 'Gold Book'), http://goldbook.iupac.org (2006-) because many terms used in photocatalysis are defined in these documents.

The working party included also D. Bahnemann,[9] J. R. Bolton,[10] L. K. Koopal,[11] V. K. Ryabchuk,[4] E. Savinov. [†] [7]

[9]Institut für Technische Chemie, University of Hannover, Hannover, Germany; [10]Bolton Photosciences Inc., Edmonton, AB, Canada;[11]Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen, The Netherlands

In addition to the members of the working party, the following scientists collaborated with this Glossary: O. M. Alfano, M. Anpo, V. Augugliaro, C. Bohne, S. Esplugas, E. Oliveros, C. von Sonntag, R. G. Weiss, and M. Schiavello[†]

[†] E. Savinov and M. Schiavello are deceased.

PHOTOSENSITIZATION OF DNA BY Β-CARBOLINES: KINETIC ANALYSIS AND PHOTOPRODUCTS CHARACTERIZATION

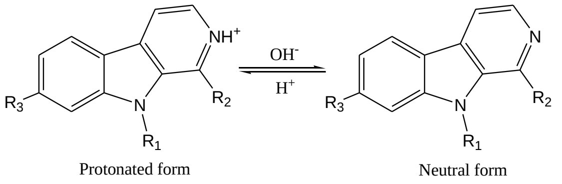
M. Micaela González[1], Mariana Vignoni[2], Matías Alés-Gandolfo[3], Magalí Pellon-Maison[4], M. del Rosario González-Baró[4], Rosa Erra-Balsells[1], Bernd Epe[5], Franco M. Cabrerizo[3]

[1] CIHIDECAR-CONICET, Fac. de Ciencias Exactas y Naturales, UBA,. Buenos Aires, Argentina. [2] INIFTA-CONICET, UNLP, La Plata, Argentina. [3] IIB-INTECH-UNSAM-CONICET, Chascomús, Argentina. E-mail: fcabrerizo@intech.gov.ar [4] INIBIOLP-CONICET, UNLP, La Plata, Argentina. [5] Johannes Gutenberg University of Mainz, Institute of Pharmacy, Mainz, Germany. E-mail: epe@uni-mainz.de

β-carbolines (βCs) are alkaloids belonging to a family of heterocyclic compounds showing in its structure the 9*H*-pyrido[3,4-*b*]indole moiety. The structures of three βC alkaloids and two of its derivatives are shown in Scheme 1. βC alkaloids are present in a wide range of biological systems and play a variety of significant photo-dependent roles.

βCs have demonstrated that can act as very good photosensitizers. Under UV-A irradiation, norharmane and harmane are able to induce chromosome damage in mammalian cells,[1] and to inactivate bacteria[2] and viruses.[3] In addition, it has been proposed that the biological role of some βCs in plants could be related with the defense response (*i.e.*, photo-toxic effects) against insects, webworms, etc. In a very recent work, we have demonstrated that photosensitized DNA relaxation by norharmane (upon UV-A excitation) takes place.[4] The later process involves, mainly, electron transfer reactions (*i.e.*, Type I mechanism). Despite their acknowledged importance, the main biological role of these alkaloids and the mechanisms involved in those processes are, to date, nevertheless still poorly understood.

In the present work, we set out to systematically examine the capability of three important βCs [norharmane (nHo), harmane (Ho) and harmine (Ha)] and two βC derivatives [*N*-methyl-norharmane (*N*-Me-nHo) and *N*-methyl-harmane (*N*-Me-Ho)] to photo-induce DNA damage, in aqueous solution phase, upon UV-A excitation. In particular, a comparative kinetic analysis was performed to evaluate the extent of the DNA relaxation made by each βC and also to find out the mechanisms involved in each case. In addition, to identify the chemical nature of the DNA-photoproducts formed upon photosensitization several experiments, using specific DNA endonucleases[5,6], were carried out. In all cases, the presence of 8-oxoguanine and apurinic/apyrimidinic sites was observed; whereas, only in the case that harmine was used as photosensitizer thymidine dimer formation could be detected.



	R_1	R_2	R_3
norHarmane	-H	-H	-H
Harmane	-H	$-CH_3$	-H
N-Methyl-norharmane	$-CH_3$	-H	-H
N-Methyl-harmane	$-CH_3$	$-CH_3$	-H
Harmine	-H	$-CH_3$	$-OCH_3$

Scheme 1. Structures of the five βCs studied and the acid-base equilibrium with $pK_a \sim 7$ in aqueous solution. The nitrogen of the indolic ring (*i.e.*, R_1=H; norharmane, harmane, and harmine) has a pK_a value greater than 12.

---

[1] K. Shimoi, H. Kawabata, I. Tomita, *Mutat. Res.* **1992**, *268*, 287.

[2] K. Shimoi, R. Miyamura, T. Mori, T. Todo, E. Ohtsuka, K. Wakabayashi, N. Kinae, *Carcinogenesis* **1996**, *17*, 1279.

[3] J.B. Hudson, E.A. Graham, G.H.N. Towers, *Photochem. Photobiol.* **1986**, *43*, 21.

[4] M. M. Gonzalez, M. Pellon-Maison, M. A. Ales-Gandolfo, M. R. Gonzalez-Baró, R. Erra-Balsells, F. M. Cabrerizo, *Org. Biomol. Chem.*, **2010**, *8*, 2543.

[5] O. Will, E. Gocke, I. Eckert, I. Schulz, M. Pflaum, H.C. Mahler, B. Epe, *Mutat. Res.* **1999**, *435*, 89.

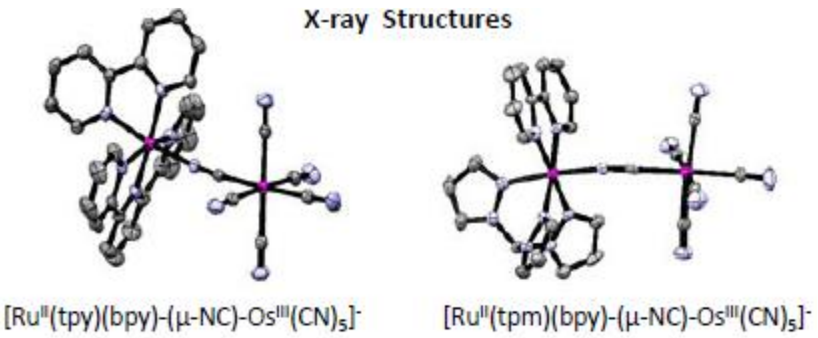
[6] H.-C. Mahler, I. Schulz, W. Adam, G. N. Grimm, C. R. Saha-Möller, B. Epe, *Mut. Res.*, **2001**, *461*, 289.

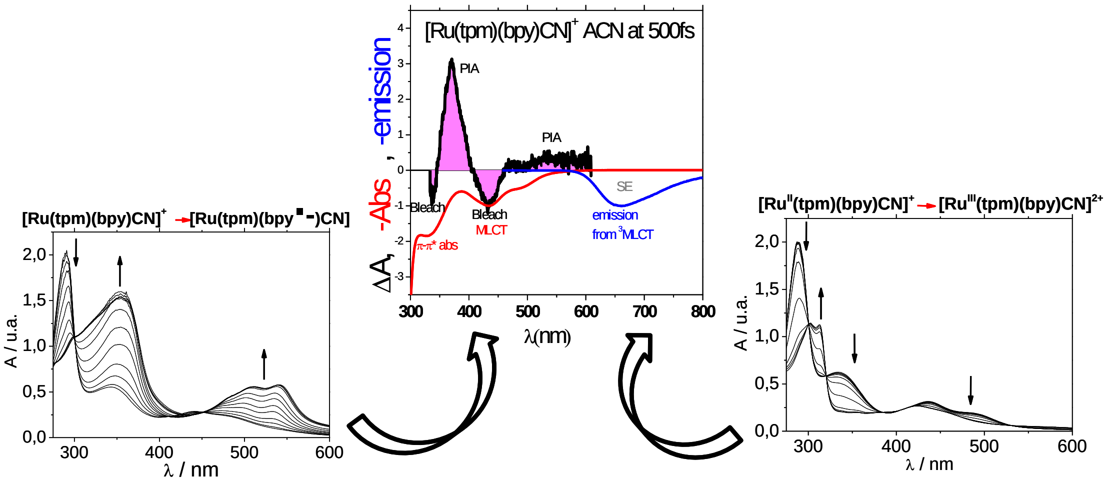
Cyanide-bridged Ru(bpy) antenna compounds: from ultrafast dynamics to solar cells

Alejandro Cadranel, **Bruno Aramburu Troselj, Luis Baraldo**
INQUIMAE & Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires,Ciudad Universitaria, Pab. II, Piso 3, C1428EHA, Buenos Aires, Argentina. e-mail: acadranel@qi.fcen.uba.ar

Since pioneering work by Bignozzi and Grätzel in the late 80's, sensitization of TiO2 with ruthenium polypiridines has been largely studied. However, although light-to-energy conversion has reached a maximum efficiency of only 11,6%, cyanide-bridged polymers have not been exhaustively explored. Synthetic difficulties and potential creation of new vibrational deactivation pathways may have decreased the interest in developing polynuclear systems.

We present two series of cyanide-bridged antenna compounds, based on [Ru(tpy)(bpy)] and [Ru(tpm)(bpy)] moieties (tpy=2,2';6',2"-terpyridine, bpy=2,2'-bipyridine, tpm=tris(1-pirazolyl)methane). Understanding their ultrafast excited state dynamics is of crucial importance to rationally design complexes of higher nuclearity that bear more than one Ru(bpy) chromophoric unit. Moreover, a new anchoring ligand is tested in dye-sensitized solar cells to evaluate its incorporation into the polynuclear compounds.





Synthesis and derivatization of Silicon nanoparticles with thiols terminated groups. Variation in the luminescent properties.

Paula Caregnato, M. Laura Dell'Arciprete, Daniel O. Mártire and Monica C. Gonzalez.

INIFTA, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP) C.C.16, Suc. 4, La Plata, Argentina (caregnato@inifta.unlp.edu.ar).

Silicon nanoparticles of 1-5 nm size (NP-Si) have received a great attention, as they combine size-dependent photoluminescence, the capacity for singlet oxygen ($^1O_2$) generation and of reducing methyl viologen, and the richness of silicon surface chemistry **[Llansola 2010]**. Remarkable properties of silicon-based nanoparticles, when compared to other materials, are their biocompatibility, biodegradability and tunable surface derivatization for drug delivery and the fact that silicic acid administered to humans is efficiently excreted through the urine **[Park 2009]**.

Thiols are extraordinarily efficient antioxidants. Humans and animals are continuously exposed to compounds with thiol and related disulfide groups, such as those present in garlic and fish. In vivo oxidation of thiols under conditions of oxidative stress, generate a group of redox-active molecules capable of oxidizing and inhibiting the biological activity of proteins and enzymes. To study the effect of surface antioxidants on the nanoparticle capacity of producing $O_2^{\cdot -}$ and $^1O_2$ radicals by photolysis, 1-2 nm size NP-Si were synthesized and derivatized with thiol-terminated groups.

The assembly method (Bottom-up) was used for the synthesis where the nucleation and growth of the particles were performed in the interior of inverse micelles **[Rosso-Vasic 2008]**. The chemisorption of organic thiols on NP-Si surface was developed according to **[Xu 2003]** and **[Caregnato 2010]**. The synthetic strategy involved the oxidiation of the particle surface and further silanization with 3-mercaptopropyltrimethoxysilane (MPTS).

The particles were characterized by their excitation–emission spectra, and by STM spectroscopy, where the modified particle size was between 0.7-2.2 nm.

The ability of the NP-SiH particles to generate $O_2^{\cdot -}$, $^1O_2$ and organic radicals upon photolysis was also measured, in order to evaluate the effect of organic surface groups in the generation of ROS.

[Llansola 2010] Llansola Portolés MJ, David Gara PM, Kotler ML, Bertolotti S, San Roman E, et al. (2010) Silicon Nanoparticle Photophysics and Singlet Oxygen Generation. Langmuir 26: 10953-10960.

[Park 2009] Park J-H, Gu L, von Maltzahn G, Ruoslahti E, Bhatia SN, et al. (2009) Biodegradable luminescent porous silicon nanoparticles for in vivo applications. Nature Materials 8: 331-336.

[Rosso-Vasic 2008] Milena Rosso-Vasic, Evan Spruijt, Barend van Lagen, Luisa De Cola and Han Zuilhof , Small (2008) 10, 1835-1841.

[Caregnato 2010] Caregnato P, Forbes MDE, Soria DB, Mártire DO, Gonzalez MC, J. Phys. Chem. C. (2010), 114, 5080-5087.

[Wu 2003] Wu X, Liu H, Liu J, Haley KN, Treadway JA, Larson JP, Ge N, Peale F, Bruchez MP. Nat. Biotechnol (2003) 21, 41-46.

Study on the photodegradation of emerging pollutants in aqueous solution under simulated sunlight: Effect of natural photosensitizers.

Luciano Carlos[1], Daniel O. Mártire[1], Juan Gomis[2], Antonio Bernabeu[2], Antonio Arques[2]

[1] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CCT-La Plata-CONICET, Universidad Nacional de la Plata, La Plata, Argentina. [2] Grupo de Procesos de Oxidación Avanzada, Departamento de Ingeniería Textil y Papelera, Universidad Politécnica de Valencia, Campus de Alcoy, Alcoy, Spain.

The presence of pharmaceutical and personal care products in surfaces waters is an emerging environmental issue. Sunlight mediated photodegradation may occur via direct or indirect reactions and may play an important role in the fate of these compounds in natural waters.

In this work, the effect of the presence of natural photosensitizers such as humic substances (HS), nitrate and Fe^{3+} on the photodegradation of a mixture of six emerging pollutants (EPs) was studied. The EPs employed in the mixture were acetominophene (analgesic), caffeine (stimulating agent), acetemiprid (pesticide), clofibric acid (fungicide), carbamazepine (psychiatric drug) and amoxycilin (antibiotic). The experiments were performed under simulated sunlight at 30-35°C and the pH was adjusted to 7. In all the experiments, 5 mg/L of each EPs was used. The concentration profiles of the EPs were followed by HPLC.

Direct photolysis of the EPs mixture showed that after 5 h of irradiation clofíbric acid, acetamiprid and amoxicillin were completely removed from the solution, while only 30% of acetaminophen, caffeine and carbamazepine were consumed. The presence of Aldrich humic acid (AHA; 5-100 mg/L) in the solutions resulted in an inner filter effect, decreasing the rate of photodegradation of the EPs. This effect was higher with increasing the AHA concentration on clofibric acid, amoxicillin and acetamiprid. In additional experiments, with different sources of SH (humic and fulvic acid from different brands), the same inner filter effect was observed. From experiments carried out at different pH (5 and 9) with 20 mg/L AHA, a significant enhancement in the consumption rate of acetaminophen and amoxicillin at pH 9 is observed, which shows that AHA photosensitizes the degradation of these substrates. On the other hand, the presence of Fe^{3+} and AHA in the EPs mixture showed a complex effect. 1mg/L of Fe^{3+} results in an increase of photodegradation rates of acetaminophen, caffeine, carbamazepine and clofíbric acid, while 5 mg/L of Fe^{3+} caused a reduction of the photodegradation rates of all EPs. Finally, for almost all the substrates, except for acetamiprid and amoxicillin the presence of nitrate ions in aqueous solutions (50 mg/L) resulted in a reduction of their consumption time.

The bimolecular sensitization of nitric oxide release from a ruthenium complex and the resorufin dye

<u>Andréia N. Carvalho</u>, Sofia Nikolaou
Departamento de Física e Química, Faculdade de Ciências Farmacêuticas de Ribeirão Preto, Universidade de São Paulo, Av. do Café s/n, 14040-903, Ribeirão Preto, SP, Brasil.

Introduction: Ruthenium(II) complexes of nitric oxide are generally more stable and they have been successfully employed as NO delivery agents, either by accessing the reduction potential of nitrosyl ligand or by light stimulation[1]. Several groups are working on different strategies based either on the coordination of sensitizing molecules to the ruthenium ion (dyes or other coordination compounds with low energy absorption bands) or on bimolecular sensitization [2]. Objectives: Studying the bimolecular sensitization between resorufin dye and the *cis*-$[Ru(bpy)_2(qui)NO](PF_6)_3$ complex (qui = quinazoline). Evaluate the possibility to incorporate the compounds into a liposomal formulation, in order to dissolve them in aqueous medium. Methods: The synthesis and characterization of the nitrosyl complex followed a described procedure [2]. Photolysis of an equimolar mixture of nitrosyl and dye in organic solution (DMSO) were performed using a diode laser tag Colibri Quantum Tech, with three lasers lines (377 nm, 447 nm and 532 nm). The electronic spectra of the photoproducts were monitored during five minutes of irradiation at each wavelength. The results were compared with that obtained in analog experiment made in absence of the resorufin dye. The vesicles, composed by L-α-phosphatidylcholine (from egg yolk) and cholesterol, were prepared by ethanolic injection method [3]. Two samples were prepared; one containing empties vesicles and the other incorporating the mixture (complex and dye). Results: The liposomes were nanometer size, being the empty vesicles smaller (65.8 nm) than the vesicles incorporating the mixture (85.7 nm). The values of zeta potential (-11.2 mV and -5.25 mV for the empty and incorporated liposome, respectively) and the low values of polydispersity (0.218 and 0.129 for the empty and incorporated liposome, respectively) suggest that the formulation is stable and that the vesicles formed are homogenous and monodisperse. Compound *cis*-$[Ru(bpy)_2(qui)NO](PF_6)_3$ displays absorptions bands in the UV region and a *ligand to metal* charge transfer band (LMCT) at 430 nm [2], with no significant absorption above 500 nm (only the tail of the LMCT band). Its irradiation at 377 nm access directly the $Ru(II)\rightarrow NO^+$ charge transfer band [2], leading to a photoproduct bearing the Ru(III) →S (solvent) chromophore, with a band at λ_{max} = 458 nm tentatively ascribed to a LMCT. Irradiating the equimolar mixture of resorufin : complex at 532 nm (strong absorption of the resorufin, superimposed with the LMCT band of the nitrosyl at 430 nm), it is observed the formation of a different photoproduct. Assuming a photoinduced energy transfer as the pathway for the sensitization of the NO release, the photoproduct of this last irradiation contains the Ru(II) →S (solvent) chromophore , which displays the MLCT transition (*metal to ligand* charge transfer) at λ_{max} = 400 nm. Conclusion: the addition of the resorufin dye to the ruthenium nitrosyl assists the formation of a photoproduct with the irradiation with visible light. In the next steps of this work the irradiation of the mixture incorporated in liposomes will be performed in order to monitor directly the formation of $NO_{(g)}$ in aqueous medium.

Acknowledgements: FAPESP and CNPq

References

[1] Marquele-Oliveira, F.; Santana, D. C.; Taveira, S. F.; Vermeulen, D. M.; Oliveira, A. R.; Silva, R. S.; Lopez, R. F.. J. Pharm. Biomed. Anal., **2010**, 53, 843-851. [2] Fornari, E. C.; Marchesi, M. S. P.; Machado, A. E. H.; Nikolaou, S.. Polyhedron, **2009**, 28, 1121-1126. [3] Kremer, J. M. H.; Van der Esker, M. W.; Pathmamanoharan; C.; Wiersema, P. H.. Biochem., **1977**, 16 (17), 3932-3935. [3] Kremer 1977.

Lapazine, a new long distance tautomeric system

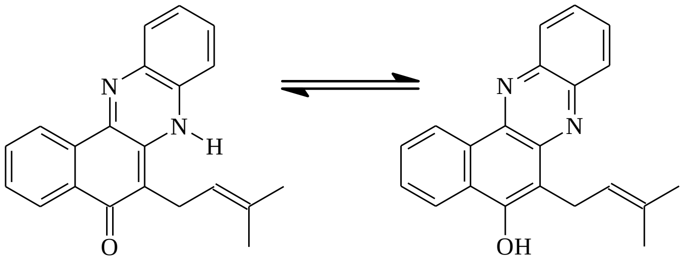
Carlos Eduardo M. Carvalho[1], Nanci C. de Lucas[1], Rodrigo J. Correa[1], Maria do Carmo F. R. Pinto[2], Eufrânio N. da Silva Jr.[3]
1-Laboratório de Fotoquímica-IQ-UFRJ; 2- Núcleo de pesquisa de produtos Naturais-UFRJ; 3- Instituto de Química- UFMG

Tautomeric systems are ubiquitous in nature and the more representative examples are the nucleic bases, purines and pyrimidines. Most tautomers exchange their protons through a pre-existing intramolecular hydrogen bond. Some rare examples have a long distance proton transfer mediated by solvent molecules. In the case of the crystal structure of the title compound, units of tautomer **I** are arranged so that an N-H---O=C hydrogen bond is present.

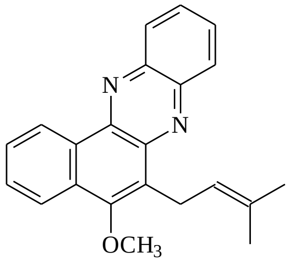
However, in non protic solvents such as hexane, only the phenol **II** is observed by absorption and fluorescence spectroscopy as determined by comparison with the methylated derivative **III**. However in protic solvents such as 2-propanol or acetonitrile both tautomers are present in solution.

Time resolved fluorescence presents only one lifetime of 0.32 ns in hexane whilst two lifetimes are observed in acetonitrile: τ_1= 0.43 ns and τ_2= 1.74 ns. The short lifetime is attributed to tautomer **II** and the longer lifetime to tautomer **I**.

A laser flash photolysis experiment was conducted, exciting the sample at 266nm, resulting in the observation of a new transient with a lifetime of 4.2 μs that was quenched by oxygen. Upon continued irradiation of the sample with laser pulses, the sample was observed to degrade and we were unable to obtain a transient spectrum.



I II



III

This work is dedicated to the memory of Prof. Antonio Ventura Pinto – NPPN, UFRJ

Glibenclamide Phototoxicity. Kinetic Study Of Photostability And Quantum Yield In Singlet Molecular Oxygen Generation, $O_2(^1\Delta_g)$

Carolina Castaño[1], **Cristina Valencia**[1], **Antonio Zanocco**[2], **Else Lemp**[2]
[1] *Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia–Sede Medellín, Medellín-Colombia, Calle 59 a No. 63-020 Nucleo del Volador, AA 568,*
gcvalenc@unal.edu.co
[2] *Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago-Chile, Olivos 1007, Casilla 233,*
azanocco@ciq.uchile.cl

keywords: glibenclamide, singlet molecular oxygen, phototoxicity.

The most actually used oral anti-diabetic for not insulin dependents patients is glibenclamide, included in Plan Obligatorio de Salud (POS) in Colombia and essential drug list of World Health Organization. Glibenclamide is consumed in long time periods with accumulative possibility in light exposed tissues, creating a high risk by use, therefore is important to study his photochemical stability, because a change in the drug molecular structure could give a decrease in his pharmacological action like the possibility to generate toxic compounds.

This drug has been reported like phototoxic and his adverse side effects include vision alterations and skin hypersensitivity in some cases. Previous studies show that in UV/VIS light drive to cultivated cervical cells and could oxidize DNA, effect that is inhibited in antioxidant presence suggesting oxygen reactive compounds participation.

Excited oxygen generation quantum yield kinetic studies and reactivity of the drug with molecular oxygen allow studying phototoxicity process by glibenclamide photosensibilization in depth. Chemical reactivity constants of 10^4 $M^{-1}s^{-1}$ order was observed, taken by steady state actinometry study facing 0.34 oxygen quantum yield, pointing an important participation of this species in phototoxicity development.

Acknowledgements
The authors are grateful with COLCIENCIAS and Universidad Nacional de Colombia-Sede Medellín under Jóvenes Investigadores e Innovadores 20101008392 program and Facultad de Ciencias for financial support and results socialization.

Quenching of Singlet Oxygen by Gadusol in Micellar Solutions

Ernesto M. Arbeloa[1,3], Sonia G. Bertolotti[2,3], and María S. Churio[1,3]
[1] Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Mar del Plata, ARGENTINA
[2] Departamento de Química, Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Río Cuarto, ARGENTINA
[3] CONICET

Gadusol (3,5,6-trihydroxy-5-hydroxymethyl-2-methoxycyclohex-2-en-1-one) is structurally related to the mycosporine-like amino acids (MAAs), a family of substances occurring in a wide variety of marine and terrestrial organisms. The high photostability of the metabolite under physiological conditions is consistent with the proposed UV-sunscreening role of the molecule in the earlier stages of life. Gadusolate, the enolate form of gadusol, efficiently quenches singlet oxygen and reduces triplet sensitizers in aqueous solution. This reactivity is in line with the results of *in vitro* determinations of the antioxidant capacity of gadusol and supports its potential role against oxidative stress in living organisms.[1,2]

With the general goal of assessing the effect of microheterogeneous media on these properties, here we report on the quenching of singlet oxygen by gadusol and gadusolate in SDS and CTAC direct micelles as simple models of the biological environments.

Singlet oxygen was generated by photosensitization with perinaphtenone. The total quenching rate constant was determined by time resolved phosphorescence detection at 1270 nm in D_2O solutions above the critical micelle concentration for each surfactant. The contribution of chemical reaction to the quenching rate was evaluated by following the substrate consumption in the micellar solution and taking the reactive quenching by gadusolate in homogeneous aqueous solution as the reference process.

The results indicate that the total quenching constants decrease between 20 to 50% in the micellar media in comparison to aqueous solution. The effect is more pronounced in the case of SDS micelles. Besides, the reactive quenching rate values also diminish relatively to aqueous solutions and with surfactant concentration.

Physical quenching seems to be less favoured in polar environments as indicated by the estimated photo-oxidation quantum yields for gadusolate: 0.50, 0.27 and 0.14 in aqueous, CTAC and SDS solutions, respectively. Thus, gadusolate appears to be more efficient in the biological-like media than in homogeneous solution where it mainly behaves as a sacrifice antioxidant.

The observations are rationalized in terms of the association of quencher to the micelle surface and the charge-transfer character of the encounter complex that it forms with singlet oxygen molecules.

[1] E. M. Arbeloa, M. J. Uez, S. G. Bertolotti, M. S. Churio. Antioxidant activity of Gadusol and occurrence in fish roes from Argentine Sea. Food Chem. (2010), 119, pp. 586–591.

[2] E. M. Arbeloa, S. G. Bertolotti, M. S. Churio. Photophysics and reductive quenching reactivity of gadusol in solution. Photochem. Photobiol. Sci. (2011), 10, pp. 133–142.

Study of the degradation of a recalcitrant dye in a laboratory reactor and in a pilot reactor by heterogeneous photocatalysis

Lucía del C. Cid[1-2], **María del C. Grande**[2], **Berta Ginzberg**[1,3]
[1] *Institute of Sanitary Engineering. Engineering School. University of Buenos Aires*
Paseo Colón 850 4º Piso (C1063ACV) Buenos Aires, Argentina.
[2] *Departament of Chemistry., Engineering School. University of Buenos Aires*
Paseo Colón 850 5º Piso, Buenos Aires, Argentina.
[3] *CONICET. National Council for Scientific and Technical Research*

Heterogeneous photocatalysis allows the degradation of recalcitrant organic compounds in aqueous solution -which can not be eliminated by traditional chemical and/or biological methods-, such as: Orange II, an azo dye, studied in this work, because it is present in wastewaters of textile, dyestuff industries, etc. In heterogeneous photocatalysis, when nanoparticles of a solid semiconductor absorb energy coming from UV-visible radiation, electron/hole pairs are generated. In aqueous solution, the holes react with water producing •OH free radicals, highly reactive, that mineralize –destroy- the adsorbed organic substances through a series of redox reactions.

In the present work titanium dioxide (TiO_2) has been used as photocatalyst, in a cylindrical, batch, slurry laboratory reactor that has been developed in our laboratory. This reactor was supplied with a coaxial UV lamp (8W, 253.7 nm), protected by a quartz jacket. Suspended particles and the oxygen needed for the reaction were obtained by bubbling air. Likewise, a cylindrical pilot reactor, that possesses an UV lamp (36 W, 253.7 nm) coaxial with it, provided with a quartz envelope, has been constructed. Air coming from a compressor was bubbled through a porous plate in the pilot reactor. Besides, two sieve plates were placed in order to keep a uniform size of bubbles. Both reactors possess the same ratio of the height of the reactor and the lamp length. Besides, they have the same optical pass and the height of the pilot reactor is fivefold the height of the lab reactor.

First, kinetics of the photocatalytic degradation of Orange II in the lab reactor for pH 7 has been studied at different concentrations of TiO_2: 1; 1.5; 2 and 2.5 g/L in order to obtain the optimal concentration of the catalyst $C_{optimal}$. This is the concentration to which all the particle surfaces are illuminated, and it must be experimentally determined for each reactor, as it depends on the design of the reactor. For this purpose, samples at different times of reaction were taken and, for each one, the concentration of Orange II was measured by means of molecular absorption UV-visible spectrophotometry. The obtained values are indicated in Figure 1:

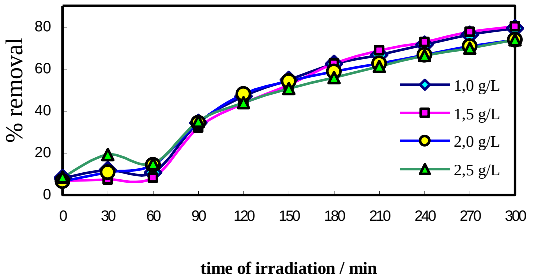
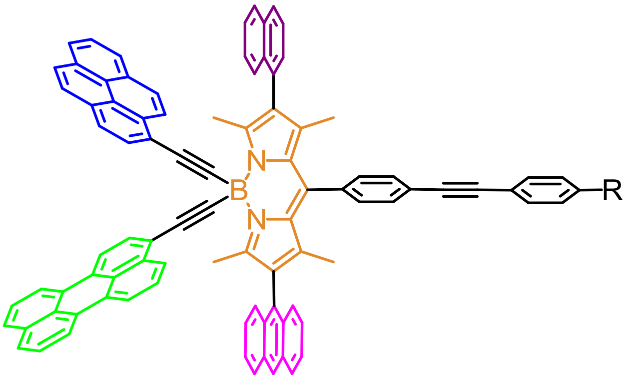


Figure 1. Photocatalytic degradation of Orange II from 20 ppm aqueous solutions in Lab Reactor.

From Figure 1, the optimal concentration of 1.5 g of TiO_2/L is determined, that is one for which the maximal degradation is achieved. With this value as reference, the kinetics of degradation in the pilot reactor was determined, obtaining similar values of degradation.

Reversible fluorescence modulation in a BODIPY-spirooxazine cassette.

Graeme Copley [a], **Devens Gust** [a]*, **Natia L. Frank** [b]*, **Daniel Plaul** [b].
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA [a] *and Department of Chemistry, University of Victoria, P.O Box 3065, Victoria, BC V8W 3V6, Canada* [b].



Measuring fluorescence from a probe molecule is an excellent, highly sensitive method for monitoring the location and environment of the probe in biomedical, nanotechnological and other applications. However, fluorescence measurements can be complicated by interference from emission of other species in the sample that results from the excitation beam. The ability to rapidly modulate emission intensity from a fluorescent probe by irradiation with light at a wavelength longer than that of the emission itself would allow phase-sensitive detection that could eliminate such interference, but is impossible to achieve with a single fluorophore. We have demonstrated that such modulation is possible by covalently linking a green-light-emitting fluorophore to a photochrome.[1] The photochrome may be photoisomerized between two forms, only one of which quenches fluorophore fluorescence via singlet-singlet energy transfer. Irradiating the molecule with modulated red light modulates the population of the molecule in the emitting state, thus modulating fluorescence intensity. One advantage of such a system is that relatively broad-band light may be used to excite fluorescence without inducing interfering emission from adventitious impurities in the sample under study. With this in mind, we have prepared fluorophores of the general type illustrated above, where the primary emitting species, a BODIPY chromophore, bears several antenna chromophores such as perylenes and pyrenes. These antennas transfer excitation energy to the BODIPY. Ultimately, the multichromophoric system must be linked to a suitable photochrome for fluorescence modulation. Several candidates are being studied, including those based on the spirooxazine framework. Properly designed spirooxazines are reverse photochromes that offer advantages in the choice of photoisomerization wavelengths, thermal reversion rates, and photostability.[2] Examples of such systems and their photochemistry will be discussed.

(1) Keirstead, A. E.; Bridgewater, J. W.; Terazono, Y.; Kodis, G.; Straight, S.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2010,** *132*, 6588-6595.
(2) Patel, D. G.; Paquette, M. M.; Kopelman, R. A.; Kaminsky, W.; Ferguson, M. J.; Frank, N. L. *J. Am. Chem. Soc.* **2010,** *132*, 12568-12586.

Concentration imaging of chlorophyll, carotenoids and anthocyanins in leaves

Gabriela Beatriz Cordon and María Gabriela Lagorio
INQUIMAE/ Dpto. de Química Inorgánica, Analítica y Química Física. Facultad de Ciencias Exactas y Naturales. Universidad de Buenos Aires. Ciudad Universitaria. Pabellón II, 1er piso, C1428EHA, Buenos Aires, Argentina. E-mails: gcordon@qi.fcen.uba.ar, mgl@qi.fcen.uba.ar

A computational vision-methodology to determine the pigments concentration in plant leaves with spatial resolution from a digital image has been developed. For this purpose, reflectance spectra of uniformly colored leaves were recorded as a first step. Reflectance spectra were obtained from 300 to 700 nm, using a spectrophotometer equipped with an integrating sphere. Barium sulphate was used as 100% reflectance (white reference). Seven reflectance spectra were averaged for each species and the resultant spectrum was used for further derivation of colour coordinates (R, G and B). The selected species were: *Hedera helix, Liquidambar styraciflua, Populus alba, Rosa sp., Gardenia jasminoides, Schefflera arboricola, Aloysia triphylla* and *Ficus benjamina*. On these leaves, chlorophyll-a, chlorophyll-b, carotenoids and anthocyanins were quantified as usual by solvent extraction and subsequent spectrophotometric measurement. Values for the RGB coordinates were calculated from reflectance spectra, and they were correlated with the pigment concentrations.

Values for the R component decreased non-linearly as chlorophyll concentration declined. Values for G component decreased linearly with chlorophyll content. Values for the B component, on the other hand resulted insensitive to chlorophyll concentration. An excellent correlation was finally found for the sum of R and G with the chlorophyll content. Other good correlations were found between the ratio R/G and the proportion anthocyanins/total chlorophyll and the ratio B/G and the carotenoids content.

On the other hand, images from another set of colored leaves were captured using a commercial scanner (HP-DeskJet F380 de Hewlett-Packard) and they were digitally processed to obtain R, G and B bands. The scanned images in TIFF format (Tagged Image File Format) with a resolution of 300 ppp and a depth of 24 bits were digitally processed using the ERDAS IMAGINE 8.4 program. Using this software the TIFF images were imported to IMG format and they were subsequently separated in R, G and B bands.

Using the correlations between the color coordinates (R, G and B) and pigments concentration, inferred from the homogeneous leaves, the concentration of pigments per pixel in the other set of leaves were estimated.

The proposed methodology allows quantifying chlorophyll-a, chlorophyll-b, carotenoids and anthocyanins in a rapid and non invasive way, thus avoiding destructive solvent extractions, which requires too much work and time in lab. Additionally, image analysis shows a great potential due to the low cost of implementation, as it merely requires a commercial scanner and an image processing program.

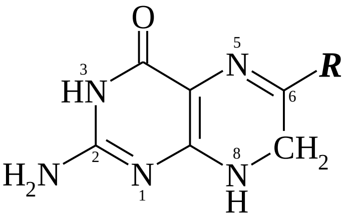
Photochemistry of 6-hydroxymethyl-7,8-dihydropterin in aqueous solution

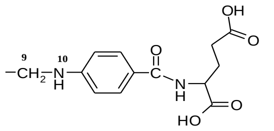
M. Laura Dántola,[1] **Esther Oliveros,**[2] **André M. Braun,**[3] **Aldana Gojanovich,**[1]
Andrés H. Thomas[1] **and Carolina Lorente**[1]
[1] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Fac. Cs. Exactas, UNLP, CCT La Plata-CONICET. CC 16, Suc. 4, (1900) La Plata, Argentina. E-mail: ldantola@inifta.unlp.edu.ar. [2] Laboratoire des IMRCP, UMR CNRS/UPS 5623, Université Paul Sabatier (Toulouse III), 118, route de Narbonne, F-31062 Toulouse cédex 9, France. [3] Engler-Bunte Institut, Karlsruhe Institute of Technology, Engler-Bunte-Ring 1, D-76131 Karlsruhe, Germany

Pterins, heterocyclic compounds widespread in biological systems, are derived from 2-aminopteridin-4(1*H*)-one or pterin. The most common pterin derivatives are 6-substituted compounds and exist in different oxidation states. They may be separated into two classes according to this property: (a) oxidized or aromatic pterins and (b) reduced pterins. Within the latter group, 7,8-dihydropterins and 5,6,7,8-tetrahydropterins are most important due to their biological activity, *e.g.* dihydrobiopterin and tetrahydrobiopterin participate in the metabolism of aminoacids,[1] tetrahydrofolic acid is a coenzyme in many reactions, especially in the metabolism of amino acids and nucleic acids.[2] All organisms require reduced folate cofactors for the synthesis of a variety of metabolites. Enzymes involved in folate biosynthesis are therefore targets for a variety of antimicrobial agents. 7,8-dihydro-6-hydroxymethylpterin-pyrophosphokinase catalyzes the attachment of pyrophosphate to 6-hydroxymethyl-7,8-dihydropterin (H_2Hmp) to form 6-hydroxymethyl-7,8-dihydropteridine pyrophosphate, an important intermediate in the biosynthesis of folate.

Little is known about the photochemical stability of H_2Hmp in aqueous solutions at room temperature and physiological pH. In this work, we describe some aspects of the H_2Hmp reactivity under UV-A irradiation. The kinetics of H_2Hmp consumption were followed by UV/vis spectrophotometry and HPLC. Hydrogen peroxide (H_2O_2) production was quantified by enzymatic methods. Products were analyzed by electrospray ionization mass spectrometry.

Excitation of H_2Hmp leads to the formation of a dimer with a molecular mass equal to exactly twice that of the substrate. The quantum yield of H_2Hmp consumption ($\Phi_{-H_2Hmp} = 0.14 \pm 0.01$) was independent of O_2 and reactant concentrations. Mechanistic and potential biological implications of the results obtained will be discussed.



R	***Dihydropterin***
$-(CHOH)_2-CH_2OH$	7,8-dihydroneopterin
$-(CHOH)_2-CH_3$	7,8-dihydrobiopterin
$-CH_2OH$	6-hydroxymethyl-7,8-dihydropterin
	7,8-dihydrofolic acid

---

[1] C. A. Nichol, G. K. Smith, D. S. Duch. *Annu. Rev. Biochem.*, **54**, 729, 1985

[2] R. Blakely, S. Benkovic, Chemistry and Biochemistry of Pterins. In: Folates and Pterins, Vol. 2. John Wiley & Sons, New York, 1984

The Photochemical Reactivity of Triplet Furan and Pyran 1,4-Naphthoquionones towards Biological Substrates

Nanci C. de Lucas[1], Rodrigo J. Corrêa[1], Simon J. Garden[1], Guilherme Santos[1], Reinaldo Rodrigues[1], Carlos Eduardo M. Carvalho[1], Sabrina Ferreira[1], José Carlos Netto-Ferreira[2], Vitor F. Ferreira[3], Paula Miro[4], M. Luisa Marin[4], Miguel A. Miranda[4].

[1]*Laboratório de Fotoquímica, Instituto de Química - Universidade Federal do Rio de Janeiro, Cidade Universitária, RJ, Brazil.* [2]*Departamento de Quıímica - Universidade Federal Rural do Rio de Janeiro, Antiga Rio São Paulo, RJ, Brazil.* [3]*Universidade Federal Fluminense, Instituto de Química, Departamento de Química Orgânica, Campus do Valonguinho, CEG, Niterói, Brazil.* [4]*Instituto de Tecnologıa Química UPV-CSIC, Universidad Politécnica de Valencia, Valencia, Spain.*

Naphthoquinones are widespread in nature and have been found in higher plants and animals as well as fungi and bacteria. Interest in these substances has intensified in recent years due to their wide range of biological and pharmacological activities where their mechanism of action can be related to redox cycling and the formation of reactive oxygen species that can damage cellular macromolecules.

Recent studies of pharmacological properties of furo- and pyrano- 1,4-naphthoquinones have revealed promising applications of these compounds.[1,2]

The photochemical reactivity towards amino acids and nucleobases or nucleosides of 15 compounds from the furo- and pyrano- 1,4-naphthoquinone series of derivatives has been examined employing the nanosecond laser flash photolysis technique. Excitation (λ = 355 or 266 nm) of degassed solutions of the 1,4-naphthoquinones, in acetonitrile, resulted in the formation of their corresponding triplet excited states. With respect to the shape of the T-T spectra, a differentiation between the furo and pyrano families is observed. These transients were efficiently quenched by L-tryptophan methyl ester hydrochloride salt, L-tyrosine methyl ester hydrochloride salt, L-α-phenylglycine methyl ester hydrochloride salt, and N- acetyl- L-tryptophan methyl ester (kq 10^9 L mol). The quantum efficiency of singlet oxygen ($^1O_2$) formation from these naphthoquinones was determined employing steady-state measurements of the phosphorescence spectrum of $^1O_2$. Very large values in all cases ($\Phi\Delta$ = 0.8-0.9) suggest a $\pi\pi^*$ character for these triplets in acetonitrile.

Low temperature phosphorescence of these naphthoquinones in methylcyclohexane revealed a band centered at ~ 700 nm that was quenched by oxygen and was attributed to the triplet. This would correspond to an energy of ~ 40 kcal/mol. Calculated values of 40-42 kcal/mol using DFT B3LYP for the furo- and pyrano- derivatives are in excellent agreement with the experimental values.

Acknowledgements: CAPES, DGU, FAPERJ, PPGQu-UFRJ.

References

1. S.B. Ferreira, F.D. da Silva, F. Bezerra, M.C.S. Lourenco, C.R. Kaiser, A.C. Pinto, V.F. Ferreira, *Archiv Der Pharmazie*, 343 (2010) 81-90.
2. F.C. da Silva, S.B. Ferreira, C.R. Kaiser, A.C. Pinto and V.F. Ferreira, *J. Braz. Chem. Soc.*, 20 (2009), 1478-1482.

A modular “Click” based approach to Optical Cation Sensors

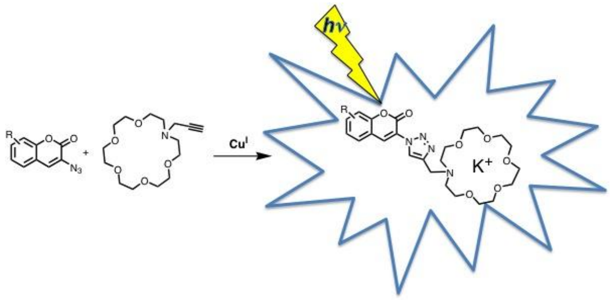
Matthew Decan and J. C. Scaiano*
The University of Ottawa, 10 Marie-Curie, Ottawa, Ontario, Canada, K1N6N5

Currently, the main methods of measuring the concentration of ions essential to plant health in soil samples are pH and electrically conductivity measurements. These two methods, however, can only give the total concentration of all ions in the sample. Given the capacity to determine specific ion deficiencies would allow for maximizing plant health and thus productivity. Robust, solid-state, ion-specific fluorescent sensors are a promising solution to the problem of measuring specific ion concentrations in soil samples.

One very successful approach to optical cation sensing makes use of photo-induced electron transfer (PET).[1] In this method a fluorescent chromophore is covalently bound to an ion-specific recognition site or ionophore. When the ionophore is ion-free the fluorescence of the chromophore is quenched by donation of an electron pair from nitrogen. When an ion is coordinated to the ionophore the electron pair is used in the coordination of the ion, the chromophore is no longer quenched and thus fluoresces.

It has been recently reported that the PET sensing mechanism can function through the 1,2,3 -triazole ring formed via Cu catalyzed “Click” reaction to quench a chromophore when an attached ionophore is free of any binding metal ion.[2] This finding opens up an excellent opportunity to create a sensor library using a modular approach to synthesis by taking advantage of the unique reactivity of click chemistry. Using a modular approach to synthesis, a large number of sensors for various metals can be obtained from a small number of azido-substituted chromophores and alkyne-modified macrocycle ionophores that are sensitive to specific ions, an example of which is shown in Figure 1. The synthesis, photophysical properties and functionality of a few such sensors developed through this modular approach will be discussed in this poster.

Figure 1:



1) Benco, J., Nienaber, H., and McGimpsey, W. G., *Sensors and Actuators B*, **2002**, 85, 126-130.
2) Tamanini, E., Katewa, A., Sedger, L., Todd, M., Watkinson, M., *Inorg. Chem.*, **2009**, 48, 319-324.

Luminescence changes upon Si-nanoparticle derivatization. A synthetic route to Al-tetracarboxyphthalocyanine funtionalized silicon nanoparticles.

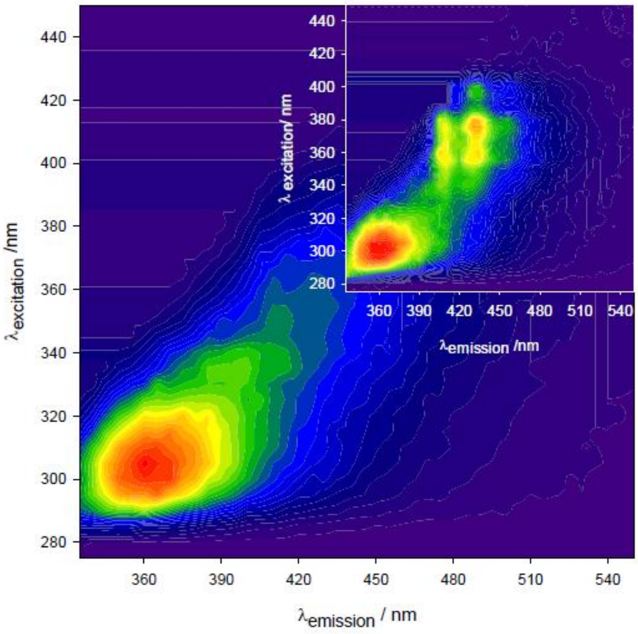
<u>María Laura Dell'Arciprete</u>[1,2], Paula Caregnato[2], Manuel Llansola[2],Lelia Dicelio[1], Mónica Gonzalez[2]

[1]INQUIMAE, Facultad de Ciencias Exactas y Naturales,UBA. Ciudad Universitaria, Pabellon 2, Piso 3 (C1428EHA) Buenos Aires, Argentina [2]INIFTA, Dpto. Química, FCE, UNLP. CC 16 Suc. 4, (1900) La Plata, Argentina

Introduction: The unique optical properties of silicon nanoparticles (SiNP), their biocompatibility, and their capability to produce cytotoxic singlet oxygen ($^1O_2$) upon UV-visible and high energy X-rays irradiation, give them great potential as therapeutic agents in photodynamic and radiotheraphy of cancer. Phthalocyanines (Pc) are well-known $^1O_2$ photosensitizers. Thus, the functionalization of SiNP with Pc is expected to present greater $^1O_2$ generation capacity than isolated SiNP or Pc. Here we report the synthesis and the funtionalization route of SiNP with Al-tetracarboxyphthalocyanine (AlTCPc), known to interact with biomolecules [1]. The IR, the UV-vis, and the photoluminescence emission-excitation spectra of the synthesis- intermediates are presented.

Experimental: The synthesis of silicon nanoparticles was performed using the reverse micelles approach [2]. Surface modification of the H-terminated Si NP with amine groups was achieved by silanization using aminoproyl-triethoxysilane (APTES) [3]. Activation of the AlTCPc is needed for coupling with the amine group of the SiNP and was carried out using N,N-dicyclohexylcarbodiimide (DCC) and N-hydroxysuccinimide ester (NHS) [4]. Incubation of NH_2 terminated Si NP with AlTCPc at room temperature yields the Si NP- AlTCPc adduct. The luminescence spectrum and decay lifetime of the functionalized Si NP were obtained with a Jobin-Yvon Spex Fluorolog FL3-11 spectrophotometer.

Results: Changes in the luminescence spectrum are observed for the different intermediate products of the synthetic route. The proposed synthetic route is shown below.

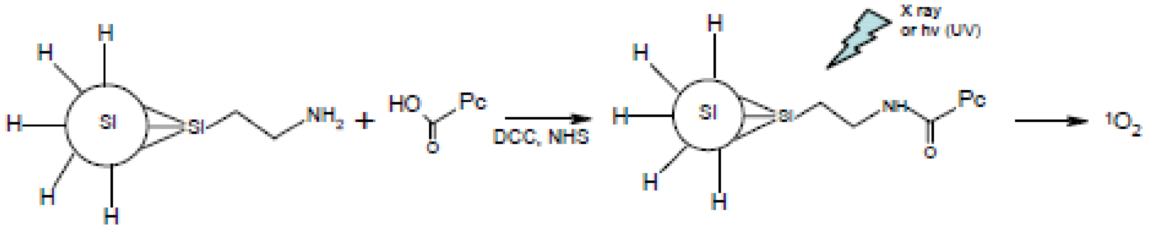


[1] Q. H. Zhou, H. M. Zhang, L. Wu, Y. Q. Wang, Protein J., 2010, 29, 265–275.

[2] M. Rosso-Vasic, L. De Cola, and H.Zuilhof, J. Phys. Chem. C, 2009, 113, 2235–2240.

[3] K.M. Kamruzzaman Selima, Y. Haa, S. Kima, Y. Changb, T. Kimc, G. Leed, I. Kanga, Biomaterials, 2007, 28, 710–716.

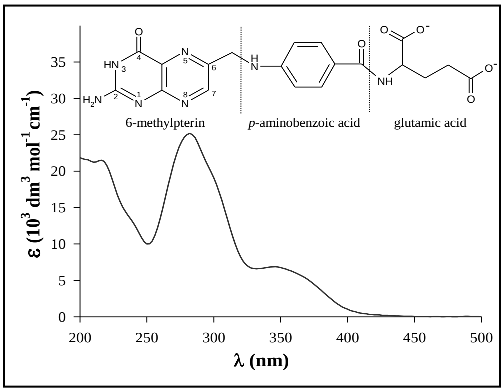
[4] I. V. Nesterova, V. T. Verdree, S. Pakhomov, K. L. Strickler, M. W. Allen, R. P. Hammer, and S. A. Soper, , Bioconjugate Chem., 2007, 18, 2159–2168.



The role of triplet states in the photooxidation of folic acid

M. Paula Denofrio,[a] **M. Laura Dántola,**[a] **Peter R. Ogilby,**[b] **Carolina Lorente,**[a,]* **and Andrés H. Thomas**[a,]*
[a] *INIFTA, Dep. de Química, Fac. de Ciencias Exactas, Universidad Nacional de La Plata, CCT La Plata-CONICET. C.C. 16, Suc. 4, (1900) La Plata, Argentina.*
[b] *Center for Oxygen Microscopy and Imaging, Department of Chemistry, University of Aarhus, DK-8000, Århus, Denmark.*

Folic acid (PteGlu) and its derivatives (folates) are conjugated pterins widespread in biological systems. Their chemical structure is composed of three moieties: 6-methylpterin (Mep), *p*-aminobenzoic acid (PABA), and glutamic acid (Glu). Folate deficiency in pregnant women has clearly been shown to be related to neural tube defects.[1] It has been proposed that one of the main functions of skin pigmentation is to avoid photolysis of folates.[2] Due to the biological implications of the photodegradation of folates in humans, the photochemical behavior of PteGlu as a model compound becomes very interesting.



In the absence of oxygen, PteGlu is photostable. However, excitation of PteGlu in air-equilibrated solutions leads to cleavage and oxidation of the molecule, yielding 6-formylpterin (Fop) and *p*-aminobenzoylglutamic acid (PABA-Glu) as photoproducts.[3,4] When an air-equilibrated aqueous solution of PteGlu is exposed to UV-A radiation, the rate of PteGlu degradation increases with irradiation time.[3,4] Analysis of this "auto-photocatalytic" effect on the basis of the general photochemical behavior of pterins[5] suggests that the reaction consists in a photosensitized process in which the photoproduct (Fop) acts as a sensitizer of its own production. The first step would involve an electron transfer from the PABA ring of the substituent of PteGlu to the triplet excited state of the sensitizer.

The aim of this work was to prove the interaction between the triplet state of unconjugated pterins and the substituent of PteGlu. With this in mind, quenching studies by means of laser flash photolysis were performed as previously described.[6] To avoid the excitation of the substrate and photolysis of the sensitizer, the experiments were carried out using Mep, a photostable unconjugated pterin, as sensitizer and PABA and PABA-Glu as quenchers. The results obtained in these flash photolysis experiments provide direct evidence for the reaction between the isolated substituent of PteGlu and the triplet state of Mep. Moreover, the values of the quenching rate constants obtained indicate a very efficient interaction. Most importantly, the data support the assumption that triplet states of oxidized pterins participate in the mechanism of the photosensitized oxidation of PteGlu.

References
[1] Mitchell, *Am. J. Med. Genet. C. Semin Med. Genet.*, 2005, **135**, 88.
[2] R. F. Branda, J. W. Eaton, *Science*, 1978, **201**, 625.
[3] A. H. Thomas, G. Suárez, F. M. Cabrerizo, R. Martino, A. L. Capparelli, *J. Photochem. Photobiol. A*, 2000, **135**, 147.
[4] M. K. Off, *et al*, *J. Photochem. Photobiol. B*, 2005, **80**, 47.
[5] M. L. Dántola *et al*, *Free Radic. Biol. Med.*, 2010, **49** (6), 1014.
[6] T. Keszthelyi *et al* , P. R. Ogilby, *Photochem. Photobiol.*, 1999, **70**, 531.

Fluorescence Quantum Yields of Water-Soluble Fraction of Crude Oil

Mariana Naspi[1,2], Adriana Mangani[1,2], Marta Susana Díaz[1,3], María Isela Gutiérrez[1,2]

[1]Departamento de Química. Facultad de Ciencias Naturales, [2]Instituto de Desarrollo Costero, [3]Departamento de Industrias. Facultad de Ingeniería. Universidad Nacional de la Patagonia San Juan Bosco, km 4, 9000- Comodoro Rivadavia, Chubut, Argentina.

The water soluble fraction (WSF) of hydrocarbons from crude oil contains molecules that have appreciable fluorescence, like polycyclic aromatic hydrocarbons (PAH) and it was found that fluorescence quantum yields vary with crude oil type. For this reason, fluorescence methods have been employed in different applications, like oil spill identification (1, 2).

In this work, we study the fluorescence of the WSF of crude oil in distilled water, seawater and their corresponding organic extracts using a crude oil from Argentine as the source of petroleum.

The sample of crude oil was from San Jorge Gulf oilfield (Chubut and Santa Cruz provinces, in south Argentine). Crude oil was placed in distilled water or in seawater obtained from a contamination free area. The sea water was filtered (pore size 0.45 μm) before used. Both samples were stirred for 6 hours and then passed through filter paper. Quantum yields were measured for distilled water and seawater directly, and for its corresponding extracts of *n*-hexane and dichloromethane. Chrysene in ethanol was used as a reference material (3). Fluorescence emission spectra and quantum yields have been measured for UV and visible excitation.

Both, fluorescence spectra and quantum yields were highly dependant on the solvent and on the excitation wavelength. Fluorescence quantum yields values varied from 10^{-2} to 10^{-1} in going from aqueous to organic solutions. The values obtained for the sample prepared in seawater were slightly lower than the values in distilled water, probably because of the interactions between solutes dissolved in seawater and fluorescent compounds from crude oil.

The results obtained could be attributed to a balance between different processes, such as energy transfer or quenching in a complex mixture and have to been taken into consideration for petroleum fluorescence applications.

(1) Østgaard K. & Jensen A. *Intern. J. Environ. Anal. Chem*, 14, 55-72, 1983.
(2) Oil Spill Environmental Forensics. Wang, Z. & Stout, S. A. (Eds.) Academic Press. San Diego, 2007.
(3) Dawson W. R. & Windsor M. W. *J. Phys. Chem.* 72, 3251-3260, 1968.

Acknowledgements:
Epsilon S.R.L. for the oil sample. SECYT-UNPSJB for financial support.

Photophysics of a novel octasubstituted zinc(II) phthalocyanine incorporated into magneto-liposomes

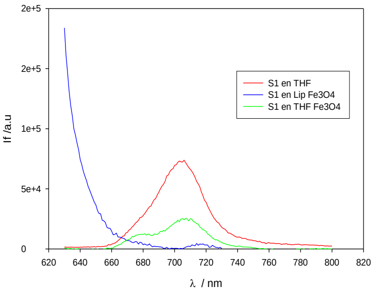
Virginia Emilse Diz[1], Julio Laurenza[1], Roberto Zysler[2], Josefina Awruch[3], Lelia E. Dicelio[1]
1INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, UBA, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina, 2Centro Atómico Bariloche R8402AGT S. C. de Bariloche, Río Negro, Argentina, 3Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, UBA, Junín 956, 1113 Buenos Aire, Argentina.

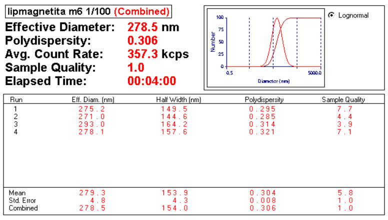
The photophysical properties of 2,3,9,10,16,17,23,24-octakis[(*N*,*N*-dimethylaminoethylsulfanyl)]phthalocyaninatozinc(II) (S1), incorporated into nanoparticles of magnetite (Fe_3O_4) and liposomes of phosphatidylcholine were studied in order to obtain magneto-liposomes as potential photosensitizer carriers for photodynamic therapy.

Fluorescence and singlet molecular oxygen quantum yields were performed in liposomes and in magneto-liposomes. S1 liposomes values were in order of $\Phi_F = 0.13$ and $\Phi_\Delta = 0.51$, whereas S1 in magneto-liposomes were $\Phi_F = 0.04$ and $\Phi_\Delta = 0.06$ respectively.

The well-dispersed liposomes were characterized by Static Light Scattering (SLS) and Transmission Electronic Microscopy (TEM). The average diameter for SLS studies was 275 nm; a reproducible unimodal population of LUV liposomes was obtained.

The incorporation of magnetite nanoparticles was established from the saturation magnetization hysteresis curves (250K); the same results were obtained for both magnetic nanoparticles and magneto-liposomes.

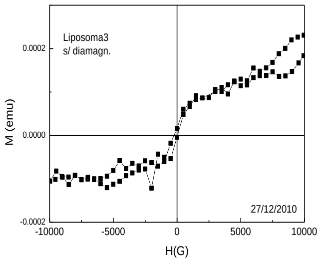




lipmagnetita m6 1/100 (Combined)

Effective Diameter: 278.5 nm
Polydispersity: 0.306
Avg. Count Rate: 357.3 kcps
Sample Quality: 1.0
Elapsed Time: 00:04:00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Sample Quality
1	275.2	149.5	0.295	7.7
2	271.0	144.6	0.285	4.4
3	293.0	164.2	0.314	3.9
4	278.1	157.6	0.321	7.1
Mean	279.3	153.9	0.304	5.8
Std. Error	4.8	4.3	0.008	1.0
Combined	278.5	154.0	0.306	1.0



References:

M. De Cuyper, M. Joniau, Eur Biophys J, 1988;15:311-319.

Virginia E. Diz, Gabriela Gauna, Cristian Strassert, Josefina Awruch, Lelia Dicelio. Journal of Porphyrins and Phthalocyanines, 2010; 14:278-283.

Photophysics of Polyfluorene Blended with a Series of Poly(alkyl methacrylate)s and Polystyrene

Raquel A. Domingues[1], **Teresa D. Z. Atvars**[1]
Institute of Chemistry, Universidade Estadual de Campinas – UNICAMP, P.O. Box 6154, Campinas, 13084-971, SP, Brazil, e-mail: rdomingues@iqm.unicamp.br

Conjugated polymers such as polyfluorenes are widely used in organic electronics as device materials (electroluminescent, photovoltaic and others). A big challenge in the development of these optoelectronic materials is to increase the device efficiency. One possible methodology particularly interesting to improve efficiency is the preparation of polymer blends which, among others effects, affects the macromolecular association of the active polymer layer[1]. Poly(alkyl methacrylate)s and polystyrene are inert materials usually used in polymeric blends for several types of electronic polymers devices. Greater device performances are obtained and may be explained by the presence of bulk heterejunction which facilities the charge transport, but also interferes with the polymer aggregation and with the morphology of every phase.

In a previous work1 using poly(9,9′-*n*-dihexyl-2,7-fluorenedilvinylene-*alt*-1,4-phenylenevinylene) (PF-PPV) and several poly(alkylmetacrylate)s we observed that the polyfluorene aggregates in mixtures whose composition was higher than 6.25 μmol L^{-1} and that the PF-PPV aggregation were more relevant when dispersed in acrylates with shorter and bulky alkyl lateral segments.

In this work we correlate the photophysical properties of polymer blends of poly(9,9-dioctylfluorenyl-2,7-diyl) end capped with dimethylphenyl (PFO) and poly(alkylmetacrylate)s by (steady state and time resolved spectroscopy in nano second time-scale) with the morphological characteristics of the mixture (by epifluorescence microscopy, scanning electron microscopy and laser confocal optical microscopy) as an attempt to understand the driven forces for the phase separation process (strongly involved with the formation of bulk heterojunction). In order to discuss the specific interaction between polyfluorene and the poly(alkylmetacrylates) we classified the acrylates according to their polarity using pyrene as sensor, assuming that the PFO molecules will be located in similar domains of the acrylate matrices. According the changes of the pyrene photophysics, the order of polarity is PMMA > PEMA > PS-*co*-PMMA > PIPMA > PS. By combining the photophysical properties and the sample morphology, we obtained that poly(ethylmetacrylate) (PEMA) was the best acrylic matrix for PFO either in terms dispersion or of chain deaggregation.

Acknowledge: Authors thanks Fapesp, CNPq and INEO/Fapesp/CNPq for financial support and fellowship

[1] European Polymer Journal 45 (2009) 2467–2477

In situ detection of reactive oxygen species using 3'-p-Aminophenylfluorescein

<u>Ana M.Edwards</u>[1], Angélica M. Garcia[1], Emilio Alarcón[2], Eduardo Lissi[3]
Facultad de Química, Pontificia Universidad Católica de Chile[1], University of Ottawa[2],
Facultad de Química y Biología, Universidad de Santiago de Chile[3].

During the last two decades, photodynamic therapy (PDT) has emerged as a potential new treatment for certain types of cancer and premalignant lesions. Photosensitizers (PS) are employed in PDT as a source of reactive oxygen species (ROS). These molecules are able to absorb light efficiently in the 400 – 700 nm region. Thus, after light absorption, photochemical processes take place mainly from the dye triplet excited state due, in part, to its large lifetime ($0.1 – 100 \times 10^{-5}$ s). Metallic phthalocyanines (MPc) stand among the most promising photosensitizers due to their intense absorption in the red region (600 – 800 nm; the "photodynamic window"), long triplet lifetimes, and large singlet oxygen quantum yields.

In the present contribution we compare the generation of reactive oxygen species by the action of light in the presence of zinc phthalocyanine (ZnPc) and Zinc hexadecafluorophthalocyanine ($ZnF_{16}Pc$) in liposomal formulations and in HeLa cells in culture. 3'-p-Aminophenylfluorescein (APF) was used as a sensor of ROS.

ZnPc and $ZnF_{16}Pc$ have a strong hydrophobic character, which promotes aggregation in high polarity media; thus, they need delivery systems for their incorporation into cells and tissues.

ZnPc and $ZnF_{16}Pc$ incorporated into dipalmitoylphosphatidylcholine (DPPC) vesicles were irradiated with red light in the presence of APF, and the fluorescence of the fluorescein generated by the APF oxidation was detected at 518 nm. The fluorescence induced by the $ZnF_{16}Pc$ irradiation was 30% higher than that induced by the ZnPc irradiation.

When sodium azide was added to both systems, a 93.3 % and 60.4 % decrease in the fluorescence was observed for ZnPc and $ZnF_{16}Pc$, respectively. These results and the fact that when D_2O was used as solvent an increase of 59% and 34% in the fluorescence was detected for ZnPc and $ZnF_{16}Pc$, respectively, indicate the participation of singlet oxygen in both systems. On the other hand, the addition of DMSO induces a 6% and 4% decrease for ZnPc and $ZnF_{16}Pc$, respectively, indicating a low participation of hydroxyl radical.

ZnPc and $ZnF_{16}Pc$ incorporated into DPPC vesicles were added to HeLa cells in culture and incubated for 90 min. The added culture medium was replaced by normal medium and the cells were irradiated with red light in the presence of APF and the fluorescence of the fluorescein generated by the oxidation of APF was detected immediately after irradiation.

The results indicate that both intracellular ZnPc and $ZnF_{16}Pc$ generate ROS, with a slightly higher effect for $ZnF_{16}Pc$.

When ZnPc and $ZnF_{16}Pc$ were incorporated to dimyristoyl phosphatidyl choline (DMPC), and then incorporated to the cells as described above, the generation of ROS by the intracellular ZnPc was similar to that observed when it was incorporated to DPPC; however, the generation of ROS by $ZnF_{16}Pc$ was considerably lower. This could be due to the fact that $ZnF_{16}Pc$ presents a higher aggregation degree in DMPC than in DPPC.

Photochemical studies of xanthene dyes in the presence of substituted phenols

M. Victoria Encinas, Andrea Valdebenito, Eduardo Pino and Eduardo Lissi.
Facultad de Química y Biología, Universidad de Santiago de Chile, Chile.

Xanthene dyes are very convenient visible photosensitizers due to their high absorption in the region 500-580 nm, and their wide solubility range. These compounds are widely used as sensitizers in many and different processes that require the use of visible light. Among these processes can be mentioned the photopolymerization of vinyl monomers, phototherapy, photosensitizing agent for biological species. More recently, they have acquired special importance as fluorescent probe to characterize biochemical and biological systems in *vitro* and also in *vivo*. It is known that the spectroscopic and photophysic behaviour of xanthene dyes is highly dependent on the nature of substituents at the xanthene ring, medium properties, and pH. Excited states of xanthene dyes are deactivated by many compounds through a photoinduced electron transfer process, where the dye acts as electron acceptor generating the radical derived from the electron donor. Thus, the systematic photochemical study of these dyes under the conditions of the process where they will be employed is important to predict their efficiencies, and improve their uses.

In this work, we studied the spectroscopic and photochemical behavior of xanthene dyes, in particular eosin, in the presence of several 4-substituted phenols in different solvents.

Singlet and triplet excited states are deactivated by phenols bearing electron donor substituent at the 4-position. Triplet quenching rate constants reached the diffusion controlled value only for compounds bearing strong electron substituents and in aqueous solutions. These values are one order of magnitude lower in acetonitrile. The deactivation of the singlet excited state involves dynamic and static quenching. Dynamic quenching rate constant values correspond to a diffusion controlled process and slightly decrease in solvent of lower polarity. The quenching rate constants and static quenching constants are strongly dependent on the electron acceptor-donor ability of the 4-substituent. A different behavior was found for phenols with electron acceptor substituents. In this case, the dye is bleached. The bleaching leads to a ground state association complex. Equilibrium association constants are related to the reduction potential of phenols. Also, the association is highly dependent on the solvent properties, thus in protic solvents is almost negligible. This behavior was also found for Rose Bengal and erythrosin.

The photochemical behavior of xanthene excited states in the presence of phenols is discussed according to electron transfer theories. Solvent effects are interpreted in terms of the solvatochromic model of Kamlet, Abboud and Taft.

Acknowledgements: Fondecyt (grant # 1070123) for financial support.

Molecular structure and medium effect on cinnamics and ionic liquid cinnamates photochemistry

Maria L. Salum, Cecilia J. Robles, Rosa Erra-Balsells
CIHIDECAR – CONICET, Departamento de Química Orgánica, FCEN, UBA. Pabellón II, 3er Piso, Ciudad Universitaria (1428), Buenos Aires, Argentina. erra@qo.fcen.uba.ar

Cinnamic acids exists in both E (trans) and Z (cis) forms in the nature. The interest in both cinnamics has increased because they were detected in plant derived products such as foods, herbs medicines, cosmetics etc. Z-Forms are not commercially available and it is quite difficult their isolation from the E/Z natural mixtures extracted from plant tissues. Recently we described a highly efficient one-pot preparation-isolation of Z-cinnamic acids (Z-CHA) by photoisomerization of the ionic liquid (IL) of E-cinnamic acids (E-CHAm; E-cinnamates). Thus we were able to conduct a comparative study of the photochemical and thermal stability of cinnamic Z/E pairs as well as that of the corresponding ionic liquids (cinnamates) Z/E pair. Although some years ago trans-cis photoisomerization and photodimmerization of naturally occurring cinnamics were the object of several investigations, few photophysical studies have been conducted on the E-isomers, and practically no studies on the corresponding Z-forms. In our hands, fluorescence could not be detected for the non substituted Z- and E-cinnamic acid pair. On the contrary cinnamics with electron donating groups at the para and meta position showed fluorescence with $\Phi f \sim 10^{-3} – 10^{-4}$ ($\tau f < 10$ ps) and Φf E > Φf Z, as well as a clear and selective effect of the presence of water in the medium on the absorption spectra of the Z-isomers (blue shift of $\lambda_{max} \sim 10$ to 30 nm). This medium effect was minimum on Z-cinnamic cid and maximum on hydroxy- and methoxy-Z-cinnamics. The ionic liquid (IL) pairs E-CHAm/Z-CHAm showed a peculiar behavior. The absorption λ_{max} (MeOH) for E-CH and E-CHAm were quite similar while λ_{max} (MeOH) for Z-CH and Z-CHAm were quite different (Fig. 1). For our surprise, the absorption λ_{max} (MeOH) for Z-CHAm was similar to the λ_{max} (H_2O) for Z-CH. Thus, a clear H_2O effect on the molecular structure of substituted Z-CH should be operating similarly to that of the amine moiety (Am) on the Z-CHAm studied Fig. 1)

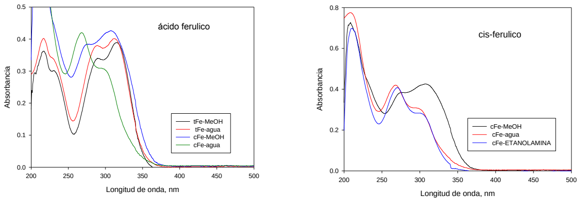
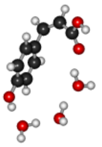
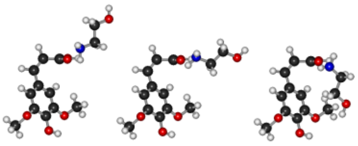


Figure 1: Absorption spectra: (left) *E*-CH and *Z*-CH (MeOH and H_2O); (right) Z-CH (MeOH and H_2O), and Z-CHAm (MeOH).

Ab initio geometry optimization and semi-empirical electronic structural calculations were used to estimate the excited state energy for both *E* and *Z* forms of all the cinnamics (CH) and IL cinnamates (CHAm). These calculations predict that the optimum geometry for Z-CH in H_2O is formed as an adduct with two and/or three H_2O molecules (bellow, left) with similar structure than the optimum obtained for IL cinamates (*Z*-CHAm) (bellow, right):



Z-CH in H_2O



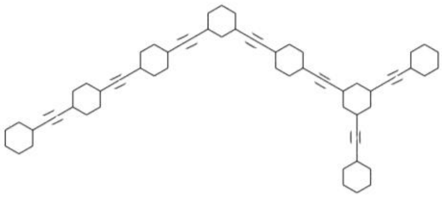
Z-CHAm; Am=$HO(CH_2)_2NH_2$

Nonadiabatic Excited-State Molecular Dynamics modeling energy transfer in light-harvesting dendrimers

<u>Sebastian Fernandez-Alberti</u>*, Valeria D. Kleiman†, Sergei Tretiak¶, and Adrian E. Roitberg||

**Universidad Nacional de Quilmes, Roque Saenz Peña 352, B1876BXD Bernal, Argentina, †Department of Chemistry and Center for Chemical Physics, University of Florida, Gainesville, Florida 32611,¶ Theoretical Division, Center for Nonlinear Studies (CNLS), and Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory, Los Alamos, NM 87545, USA || Quantum Theory Project, Department of Chemistry, University of Florida, Gainesville, Florida 32611*

Excited state nonadiabatic molecular dynamics is used to study energy transfer in dendrimer building blocks, between two-, three- and four-ring linear poly-phenylene-ethynylene units linked by meta-substitutions.



Upon excitation, dendrimers with these building blocks have been shown to undergo highly efficient and unidirectional energy transfer. The simulations start by initial vertical excitation to excited states mainly localized on the two-ring linear units. We observe ultrafast directional electronic energy transfer, corresponding to sequential two-ring→three-ring→four-ring transfer. The electronic energy transfer is concomitant with vibrational energy transfer through a dominant C≡C stretching motion. Upon $S_{n+1} \rightarrow S_n$ population transfer, a rapid increase of the S_{n+1}-S_n energy gaps and decrease of the corresponding values for S_n-S_{n-1} gaps are observed. In consequence, the S_{n+1} and S_n states become less coupled while the S_n and S_{n-1} become more coupled. This behavior guarantees the successful $S_{n+1} \rightarrow S_n \rightarrow S_{n-1}$ unidirectional energy transfer associated to the efficient energy funneling in light-harvesting dendrimers.

"Nonadiabatic molecular dynamics simulations of the energy transfer between building blocks in a phenylene ethynylene dendrimer" S. Fernandez-Alberti, Valeria D. Kleiman, S. Tretiak, and Adrian E. Roitberg, J. Phys. Chem A, 113, 7535-7542, (2009).

"Unidirectional energy transfer in conjugated molecules: the crucial role of high frequency C(triple)C bonds" S. Fernandez-Alberti, Valeria D. Kleiman, S. Tretiak, and Adrian E. Roitberg, J. Phys. Chem. Lett. 1, 2699-2704. (2010).

"The NA-ESMD modeling of photoinduced dynamics in conjugated molecules", T. Nelson, S. Fernandez-Alberti, V. Chernyak, A. E. Roitberg, and S. Tretiak, J. Phys. Chem. B, special issue "Mukamel Festschrift", Publication Date (Web): January 10. (2011)

2nd Poster session

Thursday May 19

PHOTOCHEMICAL STUDY OF $ClSO_2NCO$: COMPARISON BETWEEN GAS PHASE AND MATRIX ISOLATION RESULTS

Andrea Flores Antognini,[a] **Norma Lis Robles,**[a,b] **Rosana Mariel Romano**[b]
[a]*INQUINOA (UNT-CONICET) Instituto de Química Física, Facultad de Bioq., Quím. y Fcia., Universidad Nacional de Tucumán. San Lorenzo 456 T4000CAN, Tucumán.*
[b]*CEQUINOR (UNLP-CONICET) Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata. 47 y 115 B1900, La Plata.*

The photochemical study of species isolated in noble gases matrixes is a powerful tool for understanding photoevolutive processes in single molecules. The inert environment reduces the possibility of molecular interactions, and the vibro-rotational transitions are negligible due to the low temperatures.. In addition, the photochemistry of matrix isolated species can be assumed as a suitable model for understanding photodegradation of compounds in the atmosphere, since the dilution mimic very well the conditions to which the substances are exposed when reached by solar irradiation.

We present here the results obtained for the photochemical study of $ClSO_2NCO$ in gaseous phase and isolated in Ar matrix, stressing the differences observed using both techniques. For the gas phase experience 5 Torr of the compound were loaded *in vacuo*, into a cross-shaped glass cell equipped with quartz and CsI windows, to allow the measurement of the IR spectra during the UV-vis irradiation. On the other hand, a gas mixture of chlorosulfonyl isocyanate and Argon, in a 1:1000 proportion, was prepared by standard manometric methods. The mixture was deposited on a CsI window cooled to ca. 10, using the pulse deposition technique. The matrix isolated FTIR spectra were recorded with resolutions of 0.5 and 0.125 cm^{-1}. The samples were exposed to broad-band UV–visible radiation ($200 \leq \lambda \leq 800$ nm) and the output from the lamp was limited by a water filter to absorb IR radiation and so minimize heating effects. The results were complement by quantum chemical calculations at the B3LYP and MP2 levels of theory and employing the 6-31+G(d) and aug-cc-pVDZ basis sets.

The IR spectra taken before and after irradiation have revealed the decay of the bands belonging to the parent molecule, and the appearance and growth of new absorptions corresponding to different products. To identify these bands and help to establish the photochemical mechanisms, the integrated intensities of the new absorptions have been plotted as a function of the irradiation time. In the gas phase experiences, the photoproducts were destilled from the cell, and IR spectra of compounds of different volatility were taken to identify the species.

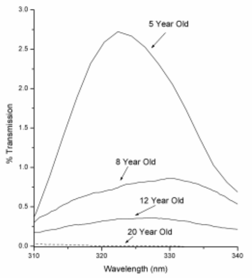
As it was expected, in the gaseous phase only stable moelcules such as SO_2 and CO were observed as volatile products. The IR spectra of the non-volatile species were interpreted in terms of dimeric and trimeric forms. In the matrix experiment, not only SO_2 and CO were identified but also the presence of ClNCO and $ClCO^{\cdot}$ radical. The comparison of our experimental vibrational spectra with data reported for SO_2 as a monomer isolated in argon matrixes indicates a certain degree of perturbation for the expected vibrational frequencies. Such perturbations were attributed to molecular complexation. Quantum chemical calculations for feasible $ClNCO\cdots SO_2$ complexes support this assumption.

The extreme dilution conditions do not favor the existence of more than one isolated molecule on a matrix site. For these reason only unimolecular processes are observed in matrix conditions. In the gas phase, the presence of bands in the C=O region suggests the formation of molecular aggregates, like dimers or trimers.

Transmission of Light to the Young Primate Retina: Possible Implications for the Formation of Lipofuscin

Elizabeth R. Gaillard[1,2], **John Merriam**[2], **Lei Zheng**[2] **and James Dillon**[1,2]
[1]*Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Il 60115*
[2]*Department of Ophthalmology, Columbia University, New York, NY 10032*

The transmission properties of the anterior segment of the primate eye change dramatically with age. For wavelengths longet than 300 nm, these properties are primarily controlled by the UV-filter compound 3-hydroxykynurenine-O-β-glucoside (3-HKG) which is synthesized in the last trimester of gestation. This compound has an absorption minimum at ca. 320 nm and a maximum at ca. 365 nm and is synthesized in the last trimester of gestation. We have developed a simple method to measure the optical properties of intact eyes and have collected data from approximately 30 human and rhesus macaque cadaver eyes of varying donor ages. We also report on measurements made in a limited (ca. six) living human eyes. The 3-HKG absorption minimum at 320 nm allows transmission of UV-B to the retina. However, as age increases, the lens absorbs increasingly more light at wavelengths longer than 400 nm, which causes it to yellow, and the window of transmission at 320 nm closes within the second or third decade. The age related rate of decrease in the transmission of blue light to the retina was similar to the rate of increase of lipofuscin formation in the retina. This observation that UV-B is transmitted to the retina may correlate with the observed rapid increase in retinal lipofuscin in children and young adults and strongly suggests that children should have high quality eye protection from sunlight especially in highly reflective environments.



Quenching of polypyridyl Cr(III) complexes excited states by Tryptophan and Tyrosine.

P. F. Garcia, J. Toneatto, G. A. Argüello
INFIQC, Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba. República Argentina.
e-mail: gerardoa@fcq.unc.edu.ar

The polypyridyl Cr(III) complexes have a potential use as phototherapeutic agents in photodynamic therapy (PDT). These photosensitizers exhibit the ability to induce DNA damage after reaching its excited state, and the capability of impairing the survival of irradiated bacteria.[1]

Proteins are one of the cellular constituents that are susceptible to photooxidation reactions. The photooxidation of amino acid side chains can cause significant alterations in the physicochemical properties of proteins and can subsequently lead to cellular damage. In particular, the amino acid tryptophan (Trp) and tyrosine (Tyr) are important targets in the cell, which are highly vulnerable to photodynamic action.[2]

In the present work, we deal with a systematic reductive quenching study of the luminescent excited state of $[Cr(NN)_3]^{3+}$ complexes (NN = phen, 5-Mephen, 4,7-diMephen, 3,4,7,8-tetraMephen, 5-Phphen and 5-Clphen) and $[Cr(phen)_2(dppz)]^{3+}$ by Try and Tyr in aqueous solutions.

We study the bimolecular quenching rate constants by time resolved and state stationary techniques in presence and in absence of oxygen. The results show that the system is a dynamic quenching, in which the excited state is deactivated by collisions.

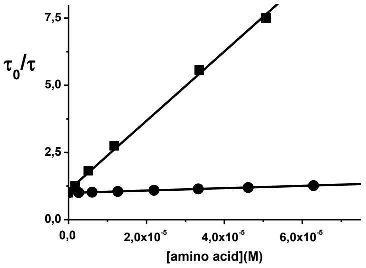


Fig. 1: Time resolved quenching rates for Tryptophan (squares) and Tyrosine (circles) by ***[Cr(phen)₃]³⁺***

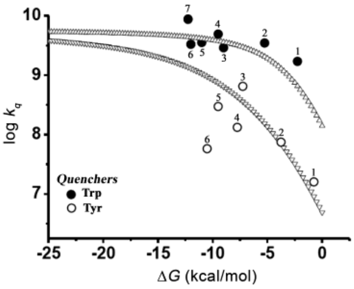


Fig. 2: Rehm Weller graphics. $[Cr(NN)_3]^{3+}$ NN= **1.** 3,4,7,8-tetraMephen; **2.** 4,7-diMephen; **3.** 5-Mephen; **4.** phen; **5.** 5-Phphen; **6.** 5-Clphen and **7.** $[Cr(phen)_2(dppz)]^{3+}$

We also see that the quenching is more effective for the Tryptophan than for the Tyrosine. The quenching constant is an order of magnitude higher for the Tryptophan (Fig. 1).

According to Rehm-Weller equation, the data obtained from log k_q vs. ΔG plot (Fig. 2) were analyzed on the basis of the current theories for electron transfer processes. The best fitting analysis yielded reorganization energies were $\Delta G^{\#}(0)$ = 62,7 and 100,3 kJ/mol for the Trp and Tyr, respectively. Te high value for $\Delta G^{\#}(0)$ are in accordance with previous works.[3]

On the other hand, we have followed the degradation of the Tryptophan by the $Cr(phen)_3^{3+}$ with fluorescence and infrared experiments at different times of photolysis. These studies indicate that the formation of products is a very little.

In sum, our results allow us to deduce that the chromium polypyridyl complexes have a high quenching efficiency, however the photodegradation indicate that the rate of escape from the solvent cage is lower than the rate of back electron transference.

[1] J. Toneatto, R.A. Boero, G. Lorenzatti, A.M. Cabanillas, G.A. Argüello, *J. Inorg. Biochem* 104 (**2010**) 697.

[2] E. Silva, V. Rückert, E. Lissi, E. Albuin, *J. Photochem. Photobiol. B Biol.*, 11 (**1991**) 57.

[3] D. Pagliero, G.A. Argüello, *J. Photochem. Photobiol. A:Chem.*, 138 (**2001**) 207.

The photo-protection strategy in aquatic environments: a facultative condition?

Patricia E. García[1], **A. Patricia Pérez**[1], **María Dieguez**[1], **Marcela Ferraro**[2] **& Horacio Zagarese**[2]**.**

[1]Laboratorio de Fotobiología. INIBIOMA. Quintral 1250. Bariloche. Argentina.
[2]Laboratorio de Ecología acuática y Fotobiología. INTECH. Chascomus. Argentina.
garcia.patriciaelizabeth@gmail.com

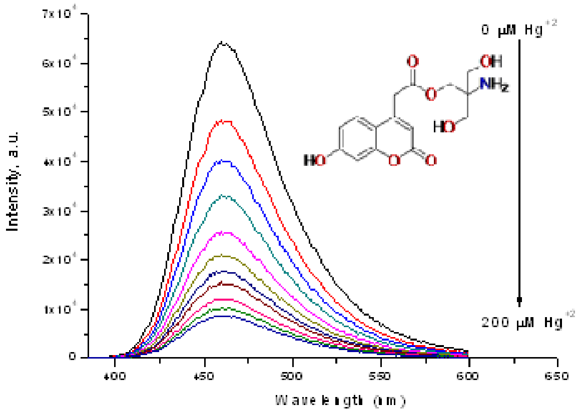
Photo-protection by pigments is one the most widespread strategies used by planktonic organisms to protect from harmful levels of Ultraviolet Radiation (UVR) (290-400 nm). This strategy includes the acquisition and/or production of chemical compounds such as carotenoids, mycosporines-like amino acids and melanins in processes regulated by light quality and temperature. In this study, we analyzed the ability of two different populations of *Boeckella gracilipes* (Crustacea: Copepoda) to bio-accumulate Mycosporine-like Amino Acids (MAAs) under PAR+UVA in a temperature gradient (5 temperatures, from 5ºC to 20ºC). Individuals of B. *gracilipes* from different lakes were use for this trial. Copepods from a population of Lake Morenito (Maximum depth of the Lake= 12m) bear naturally low MAAs concentration (3.06 ± 0.82 µg mg^{-1} D. W.) and avoid the UVR by remaining into deeper water layers during daytime. Meanwhile, copepods from the shallow mountain Lake Verde (Maximum depth of the lake= 5m, 1545 m. a.s.l) and highly expose to solar radiation have naturally much higher MAAs concentration (8.62 ± 3.19 µg mg^{-1} D.W.). HPLC analysis identified 5 different MAAs: MAA-332, Porphyra-334, Mycosporine-Glicine, Shinorine and Palithene. B. *gracilipes* from Lake Morenito has large concentration of MAA-332 but low Mycosporine-Glicine, whereas copepods from Lake Verde showed the opposite pattern. Additionally, the copepods from Lake Morenito have much higher concentration of Shinorine compare with the copepods from Lake Verde. Maximum accumulation of MAAs was observed in the trials at 8ºC in B. *gracilipes* from Lake Morenito and at 16ºC in the copepods from Lake Verde; and in both cases, there was a significant interaction between temperature and UVR. The copepods from Lake Morenito did in fact increase MAAs.

Although both copepods populations have different photo-protection strategies in their natural environment, they can be induced to accumulate MAAs through UV exposure, with different efficiency depending on temperature.

SYNTHESIS AND EVALUATION AS SPECIFIC CHEMOSENSORY Hg^{+2} OF 2-amino-3-hydroxy-2-(hydroxymethyl) propyl 2 - (7-hydroxy-2-oxo-2H-chrome-4-yl) Acetate (OGB)

Olimpo García-Beltrán[1], **Leidi C. Friedrich**[2], **José Carlos Netto-Ferreira** [3], **Víctor Vargas**[4], **Frank H. Quina**[5], **Marco T. Nuñez**[6], **Bruce K. Cassels**[7]
[1,4,7] *Department of Chemistry, Faculty of Science, University of Chile, Santiago, Chile.*
.[2,5] *Institute of Chemistry, University of São Paulo, São Paulo, Brazil.*
[2,3] *Department of Chemical Engineering, University of São Paulo, São Paulo, Brazil.*
[6,] *Institute Cell Dynamics and Biotechnology, University of Chile, Santiago, Chile.*

Molecular fluorescent chemosensing of metal ions is a promising field in chemistry with proven roles in environmental, biological and clinical applications. Hg^{+2} is a well known global pollutant and remains a danger to human health; exposure of the human body to even a low concentration of Hg^{+2} can lead to neurological diseases, various cognitive and motion disorders, and damage to the prenatal brain, digestive system and kidney.[1] This work is based on the design and synthesis of fluorescent probes that selectively complex Hg^{+2} by combining in the same molecule a very efficient fluorophore and a ligand that has high affinity and selectivity for Hg^{+2}. Compound OGB was synthesized from coumarin ethyl 2-(7-hydroxy-2-oxo-2H-chrome-4-yl) acetate[2-3]. This compound was studied for its spectral properties of absorption and emission and its photophysical properties and selectivity for Hg^{+2} fully characterized in this work. A Stern-Volmer constant of $3.3x10^5$ M^{-1} was found for the fluorescence quenching process from which a quenching rate constant of $5.6x10^{13}$ $M^{-1}s^{-1}$ could be calculated ($t_F = 5.9x10^{-9}$ s). This is a clear indication that a static quenching is occurring.



Coumarin-based fluorescent chemosensors are of great interest because of their low toxicity and easy modification. The coumarin carbonyl group plays an important role in coordinating metal ions, but most derivatives are insoluble in water. Thus, OGB has been designed by introducing multiple alcohol groups to increase its water solubility and the selectivity of the sensor to Hg^{+2}. The synthetic compound OGB is soluble in aqueous medium, selective for Hg^{+2}, and its fluorescence statically quenched by Hg^{+2}, allowing the use of OGB as a fluorosensors for this ion in tissue or water samples.

References.

1. Nisar Ahamed B., Ravikumar, I., Ghosh P. *New J. Chem*. 33:1825-1828 (2009).
2. Wang, T; Zhao, Y; Shi, M; Wu, F. *Dyes Pigments*, 75: 104-110 (2007).
3. Manvar, A; Malde, A; Verma J; Virsodia V; Mishra A; Upadhyay K; Acharya H, Coutinho E; Shah, A. *Eur. J. Med. Chem*., 43: 2395-2403 (2008).

Acknowledgment: Beca doctoral CONICYT 57090094, Proyecto ICM P05-001-F. Fellowship support from FAPESP, INCT-EMA, CEPEMA and CNPq

Nitrofluoranthene Isomer Photochemistry

Salvador Gavaldá[1], **Rafael Arce**[1],
[1]*University of Puerto Rico-RíoPiedras Campus, Department of Chemistry, PO Box 23346, San Juan, Puerto Rico, 0093I*[1]

Nitro-arenes are commonly found in airborne particles originating from combustion sources. These carcinogenic and mutagenic properties of extracts of these particles have been traced to various compounds, including high activity correlation for four-ringed nitro-arenes such as mono- and bi-substituted nitrofluoranthenes. It would be of interest to understand the possible transformation mechanisms of these compounds during transport, in order to better understand their potential effect on human health. Since these compounds are not found in the gas phase, but rather partitioned predominantly in the viscous organic phase of aerosols, and are understood to react primarily through processes initiated by photon absorption, laser flash experiments were carried out on the 1- and 3- nitrofluoranthene isomers dissolved in organic solvents. These transient spectroscopy experiments were carried out using a flash photolysis system which included a Surelite II Nd:YAG laser generating 355 nm wavelength pulses of 10 ns duration at pulse energies between 15 and 30 mJ. When dissolved in acetonitrile under nitrogen atmosphere, both isomers shows broad bands assigned to a long-lasting excited state that is quenched by the presence of oxygen or phenols in acetonitrile. The band maxima are at 505 nm for 3-nitrofluroanthene and 530 nm for 1-nitrofluoranthene in acetonitrile. High triplet quantum yields were observed for 3-nitrofluoranthene in polar, non-polar, and protic solvents. In the presence of alcohols and hydrogen donors such as those found in aerosol environment, another intermediate was observed with a band maximum at 440nm under a nitrogen atmosphere. In the presence of oxygen this intermediate was not observed. The triplet state quenching rates by phenols and other species were calculated to of the of 10^{-7} to $10^{-9}M^{-1}s^{-1}$. Steady-state photolysis experiments in which the reaction extent was folloed by HPLC/UV-Vis were also carried out for 3-nitrofluoranthene. An increased photodegradation rate was observed in the presence of alcohols and phenols. Various photoproducts were observed, including 3-aminofluorathene and small amount of reversion to the parent PAH. Aminofluoranthene production was not detected in solutions where the long lasting intermediate metioned above was not observed.

Acknowledgements: Support by the NIH SCORE (grant 5S C1ES17352-2), the SLOAN Program and the Dept. of Chemistry UPR-RP is appreciated.

Hydrolysis of quinizarin derivatives analyzed by fluorescence microscopy

Carolina Aparecida Sabatini, Marcelo Henrique Gehlen
Instituto de Química de São Carlos, Universidade de São Paulo

Enzymatic hydrolysis of quinizarin derivatives was investigated by confocal fluorescence microscopy. Quinizarin derivatives, Fig.1, are non-fluorescent, but when hydrolyzed become fluorescent. To this study, the lipase of *Rhizopus niveus* species was immobilized in a polymeric matrix. Then the quinizarin derivatives were added on enzyme/polymer film at concentration range of 10^{-9} – 10^{-12} mol L^{-1}. The enzymatic hydrolysis was monitored by images and fluorescence emission in function of time (histograms) obtained by a program linked to the microscope. The data showed that after addition of substrate, fluorescent spots begin to appear due to enzymatic activity. However, the images didn't show clear differences between the substrates. Then, the next step was the study of histograms to obtain the dynamic of quinizarin derivatives (O-CO-R; R= methyl; propyl; pentyl; heptyl). It is expected that the derivatives have different affinity for the lipase and thereby be possible to estimate their kinetic constants.

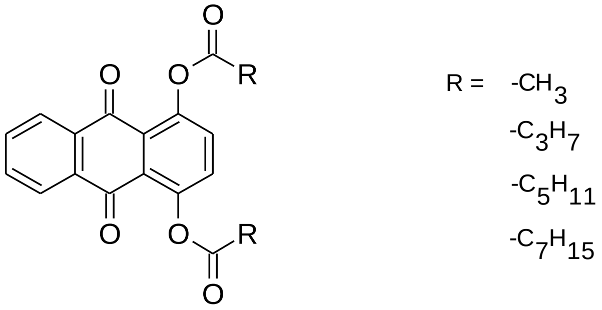


Figure 1: Chemical structure of quinizarin derivatives.

Generation of Surface Photovoltage at Porphyrin Polymer/C_{60} Interfaces

Javier Durantini[1], Matias Funes[1], Edgardo Durantini[1], Luis Otero[1], Marisa Santo[1], Thomas Dittrich[2], Miguel Gervaldo[1].

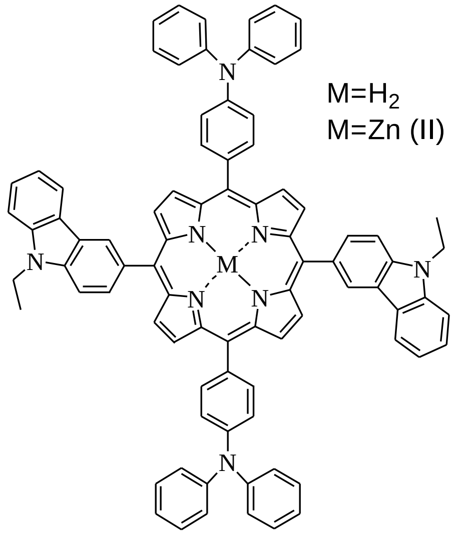
[1]Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal 3 (5800), Río Cuarto, Argentina. [2]Helmholtz Center Berlin for Materials and Energy, Institute of Heterogeneous Materials, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany.

e-mail: mgervaldo@exa.unrc.edu.ar

Interfaces between semiconductors and organic polymers are crucial for electronic properties and charge separation in devices such as organic light emitting diodes; organic field effect transistors; electrochromic systems and organic solar cells. These applications are closely related to the behavior of photogenerated charge carriers. It is valuable to investigate the surface photovoltage properties of these organic polymers since such investigation gives us information about the photogenerated charge carriers at semiconductors surface or interface, electron transfer and charge separation effect. On the other hand many studies on the development of organic optoelectronics incorporate chlorophyll derivatives and several analogues of natural pigments, such as porphyrins and phthalocyanine compounds, as light receptors and charge storage units. Donor-acceptor systems can be constructed using porphyrins and C60 Buckminsterfullerene opening up the possibility of constructing artificial photosynthetic systems in which there is a photoinduced

electron or energy transfer process from a chromophore donor to a fullerene acceptor. Furthermore, it is possible to modify the porphyrin ring with substituents with the capacity to form electropolymerized films over conducting surfaces. The electrochemical polymerization permits fine control over thickness and polymer properties; allowing to obtain stable and reproducible organic films.

In this work we report the surface photovoltage spectroscopy (SPV) of a novel porphyrin electropolymerized film. SPV is a contactless technique for characterization of semiconductors and semiconductor interfaces and the measurements are based on monitoring illumination-induced changes in the surface potential as a function of incident photon energy. Deposition of an additional C60 layer on top of the porphyrin film shows a hundredfold increase in the SPV value, showing the efficiency of this donor-acceptor system.



Real-Time Fluorimetric Degrafting Detection of Covalently Attached Fluorescent Polymer Brushes from Silica Substrates – Effects of pH and Salt Concentration

Olga Borozenko[†], Robert Godin[‡], Kai Lin Lau[†], Suzanne Giasson[†], Will Skene[†], Gonzalo Cosa[‡]
[‡]*Department of Chemistry, McGill University, 801 Sherbrooke St. West., Montréal, QC, Canada, H3A 2K6* [†]*Département de chimie, Université de Montréal, C.P. 6128, succursale Centre-Ville, Montréal, QC, Canada, H3C 3J7*

Precisely tailored surface properties of various materials can be achieved and controlled by using surface-attached polymer chains which are sensitive to external stimuli. Polyelectrolyte polymers such as poly(acrylic acid) (PAA) are especially suited for these applications as polymer conformation and physical properties are greatly influenced by the degree of ionization, which in turn is dictated by easily controllable factors such as pH, ionic strength and the presence of multivalent species.[1] Surfaces were readily functionalized with PAA by utilizing an ATRP initiator chemically bound to the substrate. However, particularly in the case of silica surfaces, there is great uncertainty regarding the sensitivity of the silica-polymer Si-O linkage, especially at higher pH and ionic strengths.[2] Unfortunately, this brings about variations and uncertainty in the polymer grafting density, which is critical to controlling the surface properties. We look to elucidate the exact conditions where these linkages are cleaved. Fluorescence spectroscopy combines the desired sensitivity with great temporal resolution, which makes it an ideal probing technique. In order to apply this technique to monitor surface-bound polymer degrafting, we developed a methodology to tag and monitor silica-supported PAA brushes with a fluorogenic BODIPY. The cleavage of the tagged polymer can thus be followed in real-time by fluorescence total internal reflection fluorescence (TIRF) microscopy and polymer degrafting kinetics are measured at different pH and ionic strengths.

(1) Wu, T.; Gong, P.; Szleifer, I.; Vlček, P.; Šubr, V.; Genzer, J. *Macromolecules* **2007**, *40*, 8756.
(2) Wasserman, S. R.; Tao, Y. T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

Imaging Free-radical Mediated Oxidation of Tocopherol-like Antioxidants in Model Lipid Membranes: Ensemble and Single Molecule Fluorescence Studies.

Robert Godin, Hsiao-Wei Liu, Katerina Krumova, Gonzalo Cosa.
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montréal, QC, H3A 2K6

New approaches are required to decipher the relevant reaction mechanisms in a lipid membrane because of its physical-chemical heterogeneity as a reaction medium. What is needed is a combination of a “reaction” probe coupled to a reporting methodology that allows one to determine precisely where the reaction occurs, what its elementary rate constant is, and where the reagents and products are situated. We have identified Single Molecule Spectroscopy as the ideal reporting methodology. In order that the power of Single Molecule techniques be applied to the vexing problems of heterogeneous kinetics associated with lipid membranes, one must use reactive fluorescent probes.

In this presentation, we will describe our efforts towards monitoring free radical reactions in lipid membranes at the single molecule level. We will present results obtained with the fluorescent probe B-TOH, a recently developed a-tocopherol like antioxidant, which readily undergoes emission enhancement upon free radical scavenging. Our studies were conducted with B-TOH embedded in surface immobilized liposomes containing dicumyl peroxide as the source of free radicals. Fluorescence lifetime imaging microscopy (FLIM) as well as wide-field total internal reflection fluorescence (TIRF) microscopy experiments have enabled us to observe fluorescence emission intensity increase upon radical-mediated oxidation of B-TOH. The scope and limitations of our studies will be addressed in this presentation.

Theoretical study on the photophysics of two metal-Phthalocyanine derivatives designed for singlet oxygen generation

Weverson R. Gomes[1], **Diesley M. S. Araújo**[1], **Antonio E. H. Machado**[1,2]
[1] *Universidade Federal de Uberlândia, Instituto de Química/Laboratório de Fotoquímica Av. João Naves de Ávila, 2121; 38408-100 Uberlândia, MG, Brazil;* [2]*Universidade Federal de Goiás, Campus Catalão, Departamento de Química; Catalão, Goiás, Brazil.*

This communication deals about the use of molecular design based on quantum mechanical calculation to support the synthesis of new metal-Phthalocyanine derivatives aiming to optimize properties useful in Photodynamic Therapy (PDT). In this work, we studied the compounds Zinc (II)-tetra-amino-Phthalocyanine (Zn(II)Pc) and Palladium (II)-tetra-amino-Phthalocyanine (Pd(II)Pc).

The ground state geometry of these compounds was optimized using the Density Functional Theory (DFT) procedure based on the B3LYP hybrid functional, without any symmetry constraints. The Lanl2dz atomic basis set was used to define all atoms. These calculations were performed in the presence of DMSO under the IEFPCM self-consistent reaction approach (SCRF). These calculations were followed by analytical vibrational frequency computations in order to verify the nature of the stationary state. The wavefunctions were tested for instabilities using “stable=opt” keyword. Also from the optimized structures, the excitation and the state diagram (singlet and triplet) were simulated using TD-DFT and the same previous parameters. All the calculations were done employing GAUSSIAN 09.

The calculated energy of the non-relaxed T_1 state of these compounds is respectively 88 and 95 kJ.mol-1 to Zn(II)Pc and Pd(II)Pc, very near the minimum energy necessary to produce $1O_2(1\Delta g)$ by sensitization. Considering that the theoretical projection is about 10% lower than the experimental data, this suggests that these metal-Phthalocyanine derivatives should present enough energy to sensitize the formation of singlet oxygen by energy transfer.

Additionally, both complexes are based on a diamagnetic metal ion, which guarantees the lengthening of the lifetime of the triplet state, favoring the process of sensitization.

To occur a singlet → triplet transition (intersystem crossing), it is necessary that the states involved have different orbital symmetries (El Sayed Rules). As Zn(II)Pc and Pd(II)Pc present adjacent orbitals with the same symmetry, $S_1 (\pi,\pi^*) \rightarrow T_1 (\pi,\pi^*)$, the population of T_1 from S_1 will occur by spin-orbit coupling, which is fully plausible considering the metal ions present in the center of the macrocycle.

Acknowledgements: To CNPq, CAPES and FAPEMIG.

Theoretical and Experimental Photophysical and Photochemical Characterization of the Compound Ethyl 3,12-Dioxopyran[3,2-a] Xanthene-2-Carboxylate

Antonio E. H. Machado[a,b], Ana M. F. Oliveira-Campos[c], Weverson R. Gomes[a], Diesley M. S. Araújo[a], Anderson J. Gomes[d], Hueder P. M. Oliveira[e]

[a]*Universidade Federal de Uberlândia – Instituto de Química, Lab. de Fotoquímica/ GFQM, Av. João Naves de Ávila 2121 – Bloco 5K; 38408-100 Uberlândia, Minas Gerais, Brazil.*

[b]*Universidade Federal de Goiás – Campus Avançado de Catalão, Catalão, Goiás, Brazil.*

[c]*Universidade do Minho, Centro de Química, Braga, Portugal*

[d]*Universidade de Brasília, Faculdade de Ceilândia, Ceilândia, DF, Brasil.*

[e]*Universidade Camilo Castelo Branco, Rodovia Presidente Dutra, km 138, São José dos Campos, São Paulo, Brazil.*

In the present communication we evaluate the photophysics and capability of a benzopsoralen analogue derived from xanthen-9-one to sensitize the singlet oxygen of singlet oxygen, using experimental and theoretical methodologies. The theoretical model built to represent the compound under study took into account the combination of discrete molecules of the solvent making intermolecular hydrogen bonds with the solute in combination with a dielectric continuum model (IEFPCM) to describe the solvation. The state-diagram obtained from a combination of CASSCF and TD-DFT calculations agrees very well with the very expressive quantum yield of singlet oxygen generation (Φ_Δ=1.00) in methanol, estimated from steady-state and time-resolved measurements, as well as the absorption and emission spectra.

Acknowledgements: For financial support from Fundação para a Ciência e Tecnologia - Portugal (I&D nº 226/9 and to CQ-UM), POCTI and FEDER. To FAPEMIG, CNPq, and CAPES, Brazilian Funding Agencies, for financial support and research grants.

Determinación de la incidencia de la radiación UV-A en la degradación y toxicidad del Ofloxacino

González P., Hidalgo M. E., Sánchez G.
Universidad de Valparaíso- Chile

Actually phothosensitization induced by drugs is a topic of great interest due to the constant increasing exposure to ultraviolet radiation (UV) reaching out the surface of our planet due to the depletion of ozone layer.

Valparaiso city is locate at 33°03´ south latitude, receives a large dose of UV radiation compared with other cities located at other latitudes. The dose of radiation increases during spring and summer in comparison to Santiago, located 33°28´ south latitude. In this city the ozone is generate as a result of industrial, vehicular and other forms of pollution, and large doses of radiation were filtered.

The solar irradiance during a summer day in Valparaiso is about 5,41mW/cm² time higher than those used in these experiments.

The interaction between UV radiation and drugs could result in deleterious effects like the decrease of the pharmacological activity and phototoxic reaction due to photoproducts or free radical species.

Currently it is important to design drugs free from side effects, for what it is necessary to identify structures and sustituents with photosensitive activity.

In this work the effect of the N-methyl-piperazine and N-methyl-oxacine sustituent ring on photodegradation and toxicity of ofloxacine was studied.

Photophysical and photochemical parameters were determined in the laboratory and the effect of pH and PBS and Ethanol on the absorption and emission spectra of ofloxacine and the photodegradation kinetics of the drug in different conditions were investigated.

The photodegradation rate constant values indicate that the process is oxygen-independent:

K atmosphere condition = $2.93 \times 10^{-3} \pm 2.97 \times 10^{-5}$ (s^{-1})
K oxygen atmosphere = $2.50 \times 10^{-3} \pm 1.44 \times 10^{-5}$ (s^{-1})
K nitrogen atmosphere = $2.80 \times 10^{-3} \pm 1.75 \times 10^{-4}$ (s^{-1})
K D_2O = $2.10 \times 10^{-3} \pm 1.03 \times 10^{-4}$ (s^{-1})

Phototoxicity studies using the red blood cell model and *Artemia salina*, showed that ofloxacine is not phototoxic (photohemolisis 3.19%) and FLD 138ppm, a result that is 19-fold higher than the concentration.

These result show that methyloxaine ring sustituent would produce a protection effect in the models studied compared with other quinolones structures.

Towards Gas Separation Via a Molecular Redox Pump

Michael Hambourger
A.R. Smith Department of Chemistry, Appalachian State University, 417 CAP Building,
525 Rivers St., Boone, NC 28608, USA

Gas separation / accumulation technologies have numerous applications for renewable energy systems. Examples include hydrogen purification for fuel cell applications, and carbon dioxide accumulation for reductive synthesis. A molecular-based redox pump, capable of accumulating gaseous species against a thermodynamic gradient, is proposed. This system is based on an oxidation-state dependent modulation of the binding affinity for gaseous ligands at a metal center. When embedded in a gas impermeable membrane, such a shuttle will be able to pump a target gas across the membrane by way of a redox loop. Gas will bind tightly in a specific oxidation state of the metal, followed by trans-membrane diffusion of the complex, and gas release via a change in oxidation state. Preliminary data exploring such a system will be presented, along with plans to use chromophore-donor-acceptor molecules to drive the trans-membrane accumulation of pressure gradients via a photochemical process.

Theoretical Study Of Reaction Mechanism Between Acetazolamide and Singlet Molecular Oxygen, $O_2(^1\Delta_g)$

Diana Henao[1], Cristina Valencia[1], Juan Carlos Santos[2].
[1] *Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia–Sede Medellín, Medellín-Colombia, Calle 59 a No. 63-020 Núcleo del Volador, AA 568,*
gcvalenc@unal.edu.co
[2] *Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales, Universidad Andrés Bello (UNAB), Av. República 275, Santiago de Chile, Casilla 233,*
jsantos@unab.cl

keywords: acetazolamide, photosensibilized photooxidation, singlet molecular oxygen.

Acetazolamide is a recognized drug by his pharmacological action like diuretic, atiepilectic and against glaucoma, however his use has side effects in eyes and skin marked like phototoxicity, because depend of dosage and don't involve immune system.

In relationship process between photostability and phototoxicity there are studies in photodecomposition by direct radiation and photosensibilized, seting out interactions involving singlet molecular oxygen. In previous studies with steady state methodologies, were evidenced that acetazolamide show weak excited oxygen photosensibilization character, with values of 0.056, 0.097 and 0.015 in methanol, ethanol and acetonitrile respectively, but is an efficient quenching of this excited species with predominant physical type interactions.

We show a theoretical study with different interaction routes, where by theoretical calculations (DFT) using Spartan Pro, Gaussian03 y Swizard, we show privileged interaction of excited oxygen with 2 and 5 acetazolamide thiadiazol ring positions, discarding singlet oxygen direct interaction mechanism with ring sulfur atom. The above in concordance with identified product and moderate solvent effect viewed for the reaction.

Acknowledgements
The authors are grateful for financial support by DIME project 20101007746 and Dirección de Laboratorios. Facultad de Ciencias and Facultad de Minas in Universidad Nacional de Colombia-Sede Medellín, for their support making the present work and result socialization.

ULTRAVIOLET B (UV-B) EFFECT IN THE PRODUCTION OF POLYPHENOLS IN *Chlorella sp* CELLS WITH ACQUIRED RESISTANCE

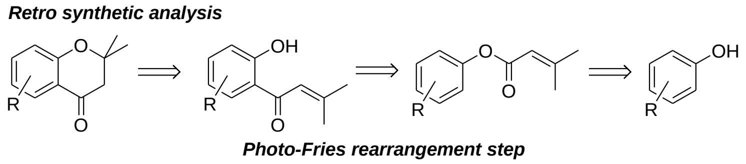
Jaime Copia[1], Hernán Gaete[1], Gustavo Zúñiga[2], María Hidalgo[1], Enrique Cabrera[1]
[1] *Facultad de Ciencias, Universidad de Valparaíso*
[2] *Facultad de Química y Biología, Universidad de Santiago de Chile*

Plants and algae are an important source of antioxidant compounds (phenols and polyphenols) as defense mechanisms against stress factors (UV radiation, temperature, herbivory). The aim of this study was to evaluate the effect of ultraviolet B radiation (UV-B) over microalgae (*Chlorella sp*) on the synthesis of photoprotective substances. *Chlorella sp* cultures were exposed to UV-B radiation (470 µW/cm2) over increasing time periods. We evaluated the total antioxidant capacity "DPPH", total polyphenols and chlorophyll "a" and "b" and cell growth in cultures exposed and unexposed. The results indicated that UV-B causes a decrease in cell density in cultures irradiated first (1 st stage), and there is an acclimation to UV-B (2 nd and 3 rd stage) only to a certain level (4 ° stage). The differences in the quantification of total phenols was statistically significant ($p = 0.00001$, $\alpha <0.05$) for the last exposition with respect to controls thus confirming that the exposure to UV-B causes an acclimation of microalgae, generating higher levels of photoprotective substances. Total antioxidant capacity and total phenols did not show a statistically significant correlation ($R2 = 0.72$) but a similar trend was observed throughout the course of the experiment. Although the amounts of antioxidant compounds were not very high, the response obtained by the microalgae Chlorella sp against UV-B, is very interesting as it could be applied to any other species in order to produce higher levels of these substances.

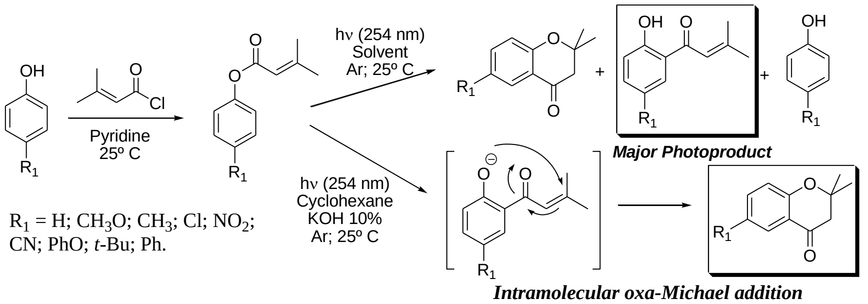
A convenient and mild photochemical reaction towards the synthesis of substituted chroman-4-ones

Daniela Iguchi, Rosa Erra-Balsells and Sergio M. Bonesi
CIHIDECAR , Depto. de Química Orgánica, Fac. de Ciencias Exactas y Naturales, UBA,
Pabellón II, 3er Piso, Ciudad Universitaria (1428), Buenos Aires, Argentina.

The chroman-4-one (2,3-dihydro-4-oxo-*4H*-1-benzopyran) ring system occupies an important position among oxygen heterocycles and features in a wide variety of compounds of biological and medicinal interest. Therefore, the vast range of biological effects associated with this scaffold has resulted in the chroman-4-one ring system being considered as a privileged structure. From a synthetic viewpoint, substituted chroman-4-ones are valued both as functional intermediates and as targets in their own right. The reported methods for the synthesis of chroman-4-ones are well documented and involve i) condensation of phenols with 3,3-dimethyl acrylic acids or its derivatives (Friedel – Craft reaction together with thermal Fries rearrangement); ii) Claisen rearrangement of propargyl ethers of phenols and, iii) Knoevenagel condensation of *o*-hydroxyphenones with aliphatic aldehydes and ketones (known as the Kabbe reaction). The last method perhaps is the most convenient and practical procedure involving the base – catalyzed condensation between a 2-hydroxyphenone and an aldehyde. However, an alternative methodology scarcely considered is the photo-Fries rearrangement reaction as a key step in the synthesis of chroman-4-ones as it is illustrated in retro synthetic approach:



Since we are interested in the application of the photo-Fries rearrangement reaction in organic synthesis, herein we report a convenient and mild photochemical reaction of a series of *para*- and *meta*-substituted esters under a one–pot base–mediated photochemical reaction to afford a variety of substituted chroman-4-one derivatives with good yield and noticeable regioselectivity. Besides, a comparative study between the photochemical reaction under homogeneous media (organic solvents: MeOH; MeCN; cyclohexane) and heterogeneous media (biphasic system) has been carried out. The following scheme illustrates our experimental results starting from the *para*-substituted phenols.



R_1 = H; CH_3O; CH_3; Cl; NO_2; CN; PhO; *t*-Bu; Ph.

The irradiations were conducted with excitation wavelength of 254 nm, at room temperature and under inert atmosphere. The photoproducts were isolated from the photolyzed solutions and were fully characterized by means of spectroscopic methods (NMR, IR, MS). In order to characterize the photo reactive electronic excited state (singlet or triplet state) photosensitization and chemical quenching were performed. Finally, the quantum yields of the photoreactions have been also measured.

In vivo Chlorophyll Fluorescence Spectroscopy in Kiwi fruit (*Actinidia deliciosa)*

Johanna Mendes Novo, Analía Iriel and M. Gabriela Lagorio
INQUIMAE/ Dpto. de Química Inorgánica, Analítica y Química Física. Facultad de Ciencias Exactas y Naturales. Universidad de Buenos Aires. Ciudad Universitaria. Pabellón II, 1er piso, C1428EHA, Buenos Aires, Argentina. E-mail:airie@qi.fcen.uba.ar

Kiwi fruit displays variable fluorescence emission from chlorophylls, similar to that observed from leaves. This behaviour is related to photosynthetic activity of tissues and its analysis has been lately used in the non-destructive diagnosis of plant health and fruit ripening.

Using a pulse modulated fluorometer Hansatech FMS1, the maximum quantum efficiency of PSII photochemistry (Fv/Fm), the quantum efficiency of photosystem II (Φ_{PSII}), and the photochemical and non-photochemical quenching coefficients (q_P and q_{NP} respectively) were determined for the whole fruit as a function of the storage time. Experiments were performed at both 4ºC and room temperature and the total storage time was 25 days. In the studied period of time, Fv/Fm slightly decreased for the chilled fruits while it diminished around 60 % for room-temperature kiwis. The parameter Φ_{PSII} decreased appreciably for both storage conditions (50% and 100% respectively). The quenching coefficients also decreased in both cases but showing high dispersion in measurements. The most sensitive parameter related to the storage time was Φ_{PSII}.

Under low photon flux irradiation at 460 nm, the whole kiwi fruit showed a non-variable emission showing peaks in the red and far red regions. This fluorescence was also detected for the flesh but it was absent in the juice. The fluorescence peaks ratio ($F_{\text{red}}/F_{\text{far-red}}$) was calculated from fluorescence spectra recorded with a PTI Quanta Master Steady-state fluorometer. This ratio showed a decrease during storage time but less important than that observed for the case of Φ_{PSII}.

The spectral distribution of fluorescence was studied for the different parts of the fruit finding different values for the fluorescence ratio ($F_{\text{red}}/F_{\text{far-red}}$) in each of them. The observed spectra were corrected for distortions due to light re-absorption processes using physical models. The results were interpreted according the relative contribution of photosystems I and II to the total observed fluorescence and they were compared with the chlorophyll emission for standard leaves.

The results obtained from the experiments based on chlorophyll variable-fluorescence allow the development of non-destructive methodologies to infer information about the kiwi state in relation to storage conditions and time.

On the other hand, the steady-state experiences led to an exhaustive comprehension of the particular features of chlorophyll fluorescence in *Actinidia deliciosa.*

Anthraquinone Derived 1,n-Diradicals: A Variety of Fates

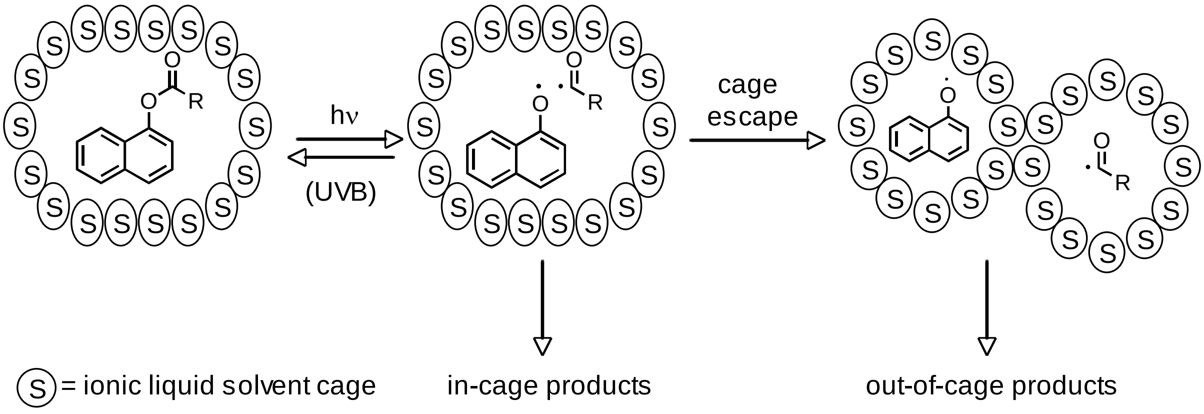
Paul B. Jones, Saurav J. Sarma, Jessica Querin, Sarah Brobeck, Thomas Rusher, Nicholas Jenkins, Alec Christian
Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109
jonespb@wfu.edu

Photolysis of 1-Alkoxy-9,10-anthraquinones gives a number of products depending on the nature of the alkoxy group, substituents on the anthraquinone and the media in which the reaction is carried out. These reactions have shown utility in the synthesis of natural products, caging of bioactive molecules and as a method for producing alkyl radicals using visible light. Attempts to find conditions under which a desired pathway can be selectively chosen, applications and mechanistic analysis will be presented.

Using the Photo-Fries Reaction as a Photochemical Probe to Quantify the Cage Effects of Ionic Liquids

Zablowsky, Amber B., Leslie, Anne A., Keirstead, Amy E.[1]
[1]*Department of Chemistry and Physics, University of New England, 11 Hills Beach Road, Biddeford, Maine, 04005, USA*

Ionic liquids (ILs) are molten salts that are liquids at or below room temperature. Their non-volatility, stability under extreme conditions, and diverse array of physical properties have made them popular "green" alternatives to conventional solvents, for applications such as dye-sensitized solar cells (DSSCs), molecular electronic devices, and various chemical processes, including synthesis and separations. While much emphasis has been placed on characterizing ionic liquids in terms of their polarity, viscosity, and diffusion properties, considerably less attention has been paid to understanding the solvent cage effects in ILs. In this work, we employ the photo-Fries reaction as a photochemical probe to examine the cage effect in the ILs [BMIM][PF_6], [OMIM][PF_6], and [BMIM][BF_4]. The photo-Fries reaction has been used to examine cage effects in a variety of heterogeneous media such as zeolites, cyclodextrins, supercritical fluids and polyolefinic films, and thus is projected to be a good probe reaction to examine this fundamental property in ILs. Our results suggest a significant cage effect in the ionic liquids compared to molecular solvents for a series of naphthyl esters. This fundamental understanding of cage effects can be combined with other known properties of ILs (such as viscosity and polarity) to better facilitate the tailoring of ILs to specific applications, including the construction of more efficient DSSCs, molecular electronic devices, and various chemical processes.



Computing Dynamic Polarizabilities and Raman Activities of Large Molecular Systems Containing Heavy Atoms: a ECP/TDDFT Based Methodology Approach

A. Khan[1], **L. N. Vidal**[2], **P. A. M. Vazquez**[1]
[1]*Instituto de Química-Caixa postal n^o 6154, Universidade Estadual de Campinas-Unicamp 13083-970, Campinas (SP), Brasil*
[2]*Departamento de Química, Universidade Técnica Federal do Paraná, Curitiba (PR), Brasil*

The quantitative agreement of theoretical dynamic Raman spectrum within experimental precision requires a large basis set (triple zeta) and the inclusion of electronic correlation at the CCSD level. These requirements limit the computations to small and medium size molecules. The development of compact polarized basis set by Sadlej had achieved gain in computational time and disk.

In order to achieve further gain in computational time and resources, our group have developed the polarized pSBKJC pseudo potential basis set to compute the optical properties of alkaline earth metals and chalcogen hydrides. Using this approach to model halogens too, in this work we present the results of a new strategy developed in our group to compute Raman activities (at 1064, 632, 514 and 488 nm excitations) for a series of organochlorinated pesticides. In this strategy, symmetry is used to automatically remove redundant configurations, the number of electrons and basis functions are reduced by using the pSBKJC pseudo-potential whose valence functions are polarized according Sadlej's method and the electronic correlation is accounted by the use of DFT (PBE0 and CAM-B3LYP functionals).

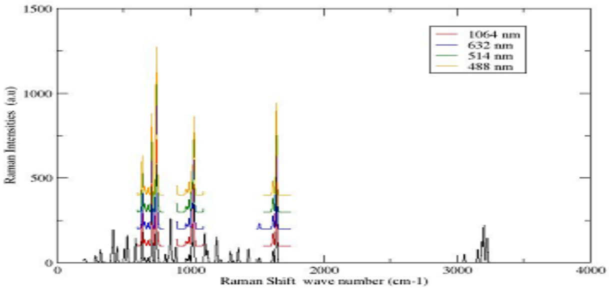


Figure: Raman spectra of TDE (DDD) Molecule using pSBKJC/DFT method at static and dynamic excited frequencies.

References

1. Vidal, L. N.; Vazquez, P. A. M. *Quím. Nova* **2003**, 26, 507
2. Vidal, L. N.; Vazquez, P. A. M. *Int J. Quantum Chem* **2005**, 103, 632
3. Vidal, L. N.; Vazquez, P. A. M. *Revista Brasileira de Aplicações de Vácuo* **2009**, 28, 21
4. Sadlej, A. J. *Collect. Czech. Chem. Comum*. **1988**, 53, 1995
5. Stevens, W. J., Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, 81, 6026

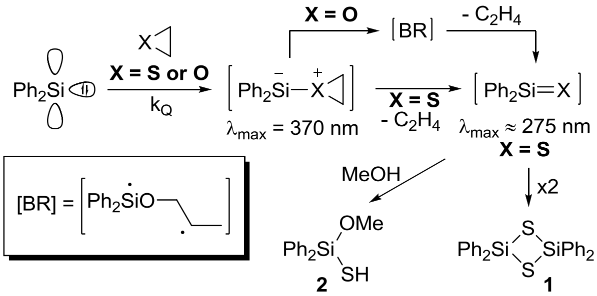
Acknowledgments:
A. Khan thanks the Conselho Nacional de Desevolvimento Científico e Tecnológico (CNPq) and Third World Academic Sciences (TWAS) for a doctoral fellowship

Photochemical Synthesis of Transient Silanones and Silanethiones by O- and S-abstraction Reactions of Transient Silylenes

Svetlana Kostina[1], William J. Leigh*[1]
Department of Chemistry and Chemical Biology, McMaster University, 1280 Main St. W, Hamilton, ON, L8S4L8, Canada[1]

Oxygen and sulfur abstraction reactions from oxiranes and thiiranes by singlet carbenes are well-known in carbene chemistry.[1] These reactions proceed through the intermediate formation of an ylide, which dissociates to form the corresponding carbonyl and thiocarbonyl compounds.[2] Oxygen abstractions from oxiranes by silylenes has been postulated to proceed by a similar mechanism, however no intermediates or products containing Si=O bonds have ever been detected.[3] Sulfur abstractions from thiiranes in solution have never been studied. The purpose of the current study is to investigate the mechanism of oxygen and sulfur abstraction reactions of dimethyl- and diphenylsilylene from cyclohexene oxide, propylene oxide and propylene sulfide at room temperature in solution, measure reaction rate constants and attempt to detect and characterize intermediates and/or products.

The results indicate that the reactions proceed via the initial formation of the corresponding silylene-oxirane (τ = 230 – 300 ns) and silylene-thiirane complexes ($\tau \leq 50$ ns), which are formed with rate constants of ca. 10^{10} M^{-1} s^{-1}. The products of the decay are invisible to our detection methods in all cases but one – the $SiPh_2$-thiirane complex. The long-lived transient product formed in this case is assigned to diphenylsilanethione ($Ph_2Si{=}S$), which has been detected and characterized for the first time. The silanethione dimerizes to the corresponding disilthiane (**1**), and reacts rapidly with methanol, t-butanol, acetic acid and n-butylamine, as do the few stable silanethiones that are known. Computational studies carried out at the B3LYP/6-311+G(d,p) level of theory suggest that cleavage of the silylene-thiirane complexes is probably concerted, while the dissociation of the silylene-oxirane complexes proceeds via 1,4-biradical intermediates, formed by initial cleavage of a C-O bond in the oxirane ring. The involvement of biradical intermediates in the reaction has been tested with a radical-clock methodology, employing a novel cyclopropyl-substituted oxirane derivative.



(1) Merrer, D. C.; Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier Science Pub Co: Amsterdam, The Netherlands, 2001; Vol. 3, p 53-113.
(2) Pezacki, J. P.; Wood, P. D.; Gadosy, T.; Lusztyk, J.; Warkentin, J. *J. Am. Chem. Soc.* **1998**, *120*, 8681-8691.
(3) Goure, W. F.; Barton, T. J. *J. Organomet. Chem.* **1980**, *199*, 33-41.

Could flavin compete with chlorophyll in the evolution of biological transformation of solar energy?

M.S.Kritsky, T.A.Telegina, M.P.Kolesnikov, Y.L.Vechtomova
A.N.Bach Institute of Biochemistry RAS, Moscow, 119071, Russia; mkritsky@inbi.ras.ru

Our objective is to substantiate the possibility of formation in evolution of a system, in which redox reactions involving excited pigment molecules lead to the conversion of photon energy into the energy-rich bonds of ATP. The postulated biochemical alternative to photosynthesis is based on the activity of flavins, i.e. the molecules structurally distant from chlorophyll, and uses other principles of organization of the antenna and reaction center.

Flavins (benzo-*[g]*-pteridines) function in organisms as coenzymes of "dark" biocatalytic reactions. Excited flavin molecules are active in energy and electron transfer processes and can photocatalyze the uphill reactions. They function as chromophores in photoenzymes DNA-photolyases and blue light-photoreceptor proteins. The widespread distribution in organic world and indispensability of metabolic functions indicate the evolutionary antiquity of flavins what is consistent with availability of these compounds (as well as structurally close pteridines) as products of chemical processes in simulated conditions of prebiotic Earth. Thermal condensation of anhydrous amino acids mixtures leads to the formation of flavin- and pteridine- conjugated amino acid polymers (proteinoids) which are aggregated in an aqueous medium to form the so-called Fox's microspheres. Formation of a pigment depended on the composition of the starting amino acids mixtures, such as replacing in (Ala, Glu, Lys) mixture of alanine to glycine, resulted in preferential accumulation of pteridines rather than flavins, what was reflected in a shift of maxima positions in the action spectrum of photophosphorylation. The molar yield of ATP, the formation of which was recorded in parallel by luciferin-luciferase assay and HPLC analysis of phosphorylation products was up to 20 % for flavin containing microspheres ($\varphi \approx 0.15 \div 0.20$), and up to 5% for the pteridine containing structures. Analysis of the photophosphorylation mechanism points to the involvement of flavin free radical molecules.

The photocycles of all flavin-binding photoreceptors include electron transfer in which the excited flavin transits to its free radical form. In DNA photolyases and cryptochromes excitation efficiency of flavin in photochemical center is enhanced by resonance transfer of energy from antenna molecules. In this role functions the other chromophore, also a coenzyme molecule, 5,10-methenyl-tetrahydrofolate or 8-hydroxy-7,8-didemethyl-5-deazariboflavin. In addition to a difference in chromophores structure, the coenzyme-binding photoreceptors differ from photosynthetic apparatus by a number of the antenna molecules serving one reaction center and the ratio of the photon-absorbing ability of the antenna's and the center's pigments. Besides, chromophores and apoproteins of these photoreceptors are polar molecules and function in aqueous, not in lipid environment.

We believe that in history of life there was a possibility of formation of the solar energy conversion mechanism alternative to chlorophyll-based photosynthesis. Considering the high sensitivity of flavins and pteridines to the UV-A and blue light, the absence of ozone shield in the atmosphere could favor the operation of such mechanism. Evolutionary advantages of the photosynthetic apparatus are its ability to consume the photons in spectral range, extending to longer wavelengths of the spectrum, as well as a higher efficiency of photon absorption by the major pigments. The analysis of the properties of excited coenzyme molecules provides an approach to understanding of the significance of structural details for their selection to the role of the chromophore in protein.

Supported by Basic Research Program N^{o} 18 of the Presidium of Russian Academy of Sciences and by grant 11-04-01007-a of the Russian Foundation for Basic Research.

Femtosecond Spectroscopy Study on Functionalized Luminescent Silicon Quantum Dots

Vincent Groenewegen, Carola Kryschi
Institute of Physical Chemistry I, Department of Chemistry and Pharmacy and ICMM,
University of Erlangen, Egerlandstr. 3, D-91058 Erlangen, Germany

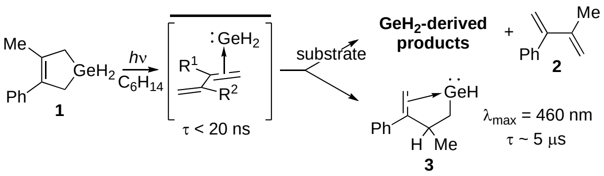
One of the central challenges in fabrication of luminescent Si quantum dots (SiQDs) tailored for nano-optolelectronics is to functionalize their surfaces with electronically efficiently coupled molecules that mediate carrier injection into the bulk and allow to optically control charge separation as well as luminescence properties of the bulk. Successful surface grafting with suitable organic compounds requires the quantitative characterization of photo-excited carrier dynamics and therewith the identification of the different pathways for photo-induced carrier transfers between electronic surface and bulk states. A nanoscopic understanding of ultrafast carrier dynamics in SiQDs on the subpicosecond time scale may be obtained through the use of femtosecond laser spectroscopy.

In this contribution we will show that the photoluminescence properties of alkenyl-passivated SiQDs may be tailored by both, core size and surface states that are efficiently coupled to resonant bulk states. Therefore, a two-step wet-chemistry synthesis route was developed which provides SiQDs with adjustable sizes and surface properties. While the energy gap of the Si core could be size-tuned by HF etching, resonant electronic surface states may be attained by hydosilylating the SiQD surface with suitable 1-ethynyl derivatives. The sizes, cristallinity and shapes as well as the surface structures of differently functionalized SiQDs were examined employing high-resolution transmission electron microscopy (HRTEM) and FTIR spectroscopy, respectively. Stationary and time-resolved photoluminescence spectroscopy experiments provided essential information of luminescent surface and bulk states. The interplay between electronically excited molecular states and conduction band states was examined upon directly monitoring photo-excited carrier dynamics with femtosecond transient absorption spectroscopy. For instance, 3-vinylthiophene, 2- and 4-vinylpyridine ligands were found to act as surface-bound antennae that mediate ultrafast electron transfer across the SiQD interface.

A Glimpse of the Chemistry of GeH_2 in Solution. Direct Detection and Characterization of an Intramolecular Germylene-Alkene π-Complex

Katie Beleznay, Paul Billone, Cameron Harrington, Lawrence Huck, and Willie Leigh
Department of Chemistry & Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, ON Canada L8S 4M1

Photolysis of 3-methyl-4-phenylgermacyclopent-3-ene (**1**) in C_6D_{12} containing acetic acid leads to the formation of diene **2**, germyl acetate (H_3GeOAc), and H_2 in yields of ca. 60%, 30%, and 20%, respectively, showing that **1** is a reasonably efficient precursor to the highly reactive parent Ge(II) molecule, GeH_2, in solution. However, the photolysis also produces a number of minor products, many of which are formally derived from hydrogermylation of the diene co-product by GeH_2, as shown by deuterium-labeling studies. Laser photolysis of **1** in hexanes leads to the formation of a transient exhibiting λ_{max} = 460 nm, which decays over ca. 20 μs with second order kinetics. It displays bimolecular reactivity consistent with that expected for a germylene derivative in most cases: oddly, however, it reacts uncharac-teristically slowly with dienes and aliphatic alkenes. The spectral and kinetic behavior of this species are inconsistent with those expected for GeH_2 on the basis of previous gas phase kinetics studies of the molecule. The species is assigned to the novel intramolecular germylene-alkene π-complex **3**, formed by a rapid solvent-cage reaction between GeH_2 and diene **2** that competes with substrate-assisted cage escape. The mechanistic conclusions and transient assignment are supported by the results of DFT calculations of the potential energy surface for the GeH_2 + **2** reaction system.

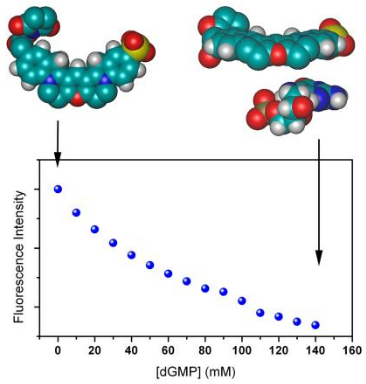


Photophysics of Single-Molecule Fluorescent Dyes

Marcia Levitus
Department of Chemistry and Biochemistry and the Biodesign Institute. Arizona State University, Tempe, AZ, USA

The growing popularity of fluorescence techniques in the biologically-related fields has generated an increasing interest in understanding how the photophysical properties of fluorescent probes are affected by their local environment when chemically attached to biomolecules. More and more, it is being recognized that the lack of such photophysical studies imposes a limitation on the amount of quantitative information that can be extracted from fluorescence measurements in biological molecules such as DNA and proteins.

Here, we present the results of an ongoing study on the photophysical properties of a series of popular fluorescent dyes in the single-molecule biophysics field. We have concentrated on how interactions with the DNA bases affect and determine the photophysical properties of the popular cyanine dyes Cy3 and Cy3B.



While the efficiency of fluorescence of Cy3 on DNA increases due to interactions with the biomolecules that increase the energetic barrier for *trans-cis* photoisomerization, Cy3B is quenched by the four nucleobases. The quenching mechanism appears to be purely static, suggesting the formation of a ground-state complex. The formation of a complex is consistent with the observed changes in diffusion coefficient in fluorescence correlation spectroscopy experiments.

On the evaluation of the number of binding sites in proteins from steady state fluorescence measurements

Eduardo Lissi(1), **Emilio Alarcón**(2) **and Elsa Abuin**(1)

(1) Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40-Correo 33, Santiago-Chile

(2) Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie. Ottawa, ON K1N 6N5, Canada

The number of binding sites for a given solute in a protein is a most relevant parameter. This number can be derived from fluorescence quenching data which provides the fraction of sites occupied at a given free solute concentration. Data are generally treated according to Scatchard´s or Ward´s equations [1]. Lately, a double logaritmic plot of the data has been extensively used with this purpose. The present communication discuss the validity of this procedure. It is concluded that this type of plot provides an evaluation of the stoichiometry of the binding process but not the number of equivalent binding sites per protein. This conclusion is validated with data obtained regarding the binding of Rose Bengal to human serum albumin [2].

References

1.- Ward L.D., Measurement of ligand binding to proteins by fluorescence spectroscopy, in Methods in Enzymology, vol. 117, 1985

2.- Alarcón E., Edwards A.M., Aspée A., Borsarelli C.D., Lissi E. A., (2009) Photophysics and photochemistry of Rose bengal bound to human serum albumin, Photochem. Photobiol. Sci. 8: 933-943

Acknowledgments

Thanks are given to Dicyt (USACH) and Fondecyt (Grants # 1070285 and #1095036)

On the evaluation of intra-protein distances between endogenous fluorophores and non-covalently bound quenchers

Eduardo Lissi and Elsa Abuin
Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40-Correo 33, Santiago-Chile

Steady state fluorescence quenching is a well established technique for the evaluation of intra-protein distances. The methodology has been widely employed for the evaluation of the distance between endogenous fluorophores (generally tryptophan moieties) and non-covalently bound quenchers incorporated into a protein. In the present communication we discuss the limitations of these measurements, establish the conditions that the system must met to allow for a meaningful evaluation of intra-protein distances, and discuss the validity of literature data derived from this type of determinations.

Acknowledgments

Thanks are given to Dicyt (USACH) and Fondecyt (Grants # 1070285 and #1095036)

Dependence of silicon nanoparticles luminescence with size and superficial oxidation

Manuel J. Llansola Portoles[1], **Reinaldo Pis Diez**[2], **Maria Laura Dell'Arciprete**[1], **Daniel O. Martire**[1], **Mónica C. Gonzalez**[1].
[1] INIFTA, Depto. Química-FCE-UNLP; [2]CEQUINOR, FCE-UNLP

Silicon nanoparticles (NP) with sizes in the range of 1 to 10 nm exhibit photoluminescence in the UV-Vis upon excitation with light of 280-400 nm. The excitation-emission spectrum depends on different factors such as size [1], superficial coating [2] and environment. However, the trends and causes of these effects still remain controversial.

In order to better understand the effect of size on the emission of NP, the emission of two sizes NP of 1.5 nm ($NP^{1.5}_{syn}$) and 3.0 nm (NP^{3}_{syn}) were compared and contrasted with the theoretical emission spectra of NP of different sizes. The geometry of NP with sizes of 0.42 nm, 0.64 nm, 0.86 nm, 1.12 nm, and 1.22 nm ($NP^{1.22}_{calc}$) was optimized using the semiempirical Density Functional Tight Binding (DFTB) method. The emission spectra were calculated at the B3LYP/LANL2DZ level of theory within the framework of the Time Depended Density Functional Theory as implemented in the FIREFLY program. Calculations for larger particles where avoided because of computational limitations. The maximum emission and excitation wavelengths (λ_{em}^{max}, λ_{ex}^{max}) measured for $NP^{1.5}_{syn}$ and NP^{3}_{syn} are (360 nm, 300 nm) and (430 nm, 370 nm), respectively. The observed size-dependent spectrum is in line with that expected for a quantum confinement-controlled Si bandstructure [1]. The theoretical calculations show that λ_{em}^{max} goes from 280 to 400 nm when the size increases from 0.42 to 1.22 nm. The experimental spectra of $NP^{1.5}_{syn}$ acceptably agree with that theoretically calculated for $NP^{1.22}_{calc}$.

To study the effect of superficial oxidation on the excitation-emission spectra, theoretical calculations were performed oxidising the $NP^{1.22}_{calc}$ particles with an oxygen monolayer. The oxidized particle structure was optimized to place the oxygen atoms in the most stable configuration. The emission spectrum of the thus oxidized particle is displaced towards higher energies with respect to that of $NP^{1.2}_{calc}$. A small displacement towards higher energy is also observed for λ_{em}^{max}. In fact, the spectrum structure resembles that of $NP^{0.86}_{calc}$. Oxidation experiments of $NP^{1.5}_{syn}$ with H_2O_2 results in an oxidized particle also showing emission in the 500-700 nm range [3] but with λ_{em}^{max} shifted to longer wavelengths.

The obtained results indicate that the combination of DFTB and B3LYP/LANL2DZ methods adequately reproduces the emission spectrum of < 1.22 nm silicon-based nanoparticles. Theoretical and experimental results on the effect of superficial oxidation are not consistent and need further investigation. Generation of surface traps may be the cause of the red shift observed in the emission of surface oxidized synthetic particles [4]. Further experiments will involve the detection of possible surface radicals by esr spectroscopy.

(1) Belomoin, G.; Therrien, J.; Smith, A.; Rao, S.; Twesten, R.; Chaieb, S.; Nayfeh, M. H.; Wagner, L.; Mitas, L. *Appl. Phys. Lett.* **2002,** *80*, 841-843.
(2) Rogozhina, E.; Belomoin, G.; Smith, A.; Abuhassan, L.; Barry, N.; Akcakir, O.; Braun, P. V.; Nayfeh, M. H. *Appl. Phys. Lett.* **2001,** *78*, 3711-3713.
(3) Belomoin, G.; Therrien, J.; Nayfeh, M. *Appl. Phys. Lett.* **2000,** *77*, 779-781.

Photophysics and photocytotoxicity of 2,9(10),16(17),22(25)-tetrakis[(2-N,N-dimethylamino)ethylsulfanyl]phthalocyaninatozinc(II) incorporated into liposomes

Noelia López Zeballos[1,2], **Julieta Marino,**[2] **María C. García Vior,**[3] **Leonor Roguin,**[2] **Josefina Awruch,**[3] **Lelia E. Dicelio**[1]

[1] INQUIMAE, Dep. de Química Inorgánica, Analítica y Química Física, Fac. de Ciencias Exactas y Naturales, UBA, Buenos Aires, [2] IQUIFIB, Departamento de Química Biológica, [3]Dep. de Química Orgánica, Fac. de Farmacia y Bioquímica, UBA, Buenos Aires.

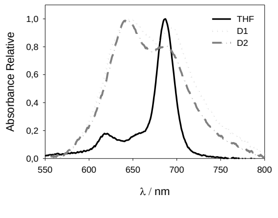
Liposomes with various lipid compositions are widely used as carriers systems for water-insoluble compounds in experimental studies and clinical trials. The extreme hydrophobicity of phthalocyanines makes necessary the use of specific carriers for their delivery into biological systems for photodynamic therapy (PDT). The presences of cholesterol in the liposome formulations enhance their mechanical stability, avoiding structural disintegration in blood.

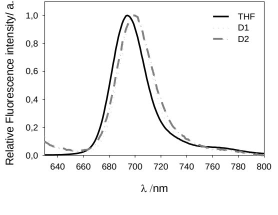
2,9(10),16(17),22(25)-tetrakis[(2-N,N-dimethylamino)ethylsulfanyl]phthalocyaninatozinc(II) (ZnPc) was incorporated into two different liposome formulations of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine, with (D1) and without cholesterol (D2). Both systems were studied in order to evaluate the photophysical properties, as well as their photocytotoxicity using human nasopharynx KB carcinoma cells.

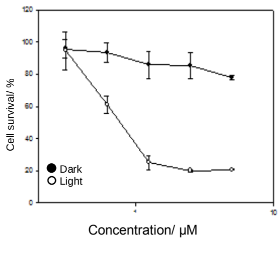
The average diameter of liposomes varied from 49.70 to 52.00 nm. The polydispersity (i.e., the measurement of size heterogeneity) for the size distribution of liposomal formulations ranged from ± 0.088 to ± 0.35. Spectroscopic characterization of free and incorporated into liposomes ZnPc absorption and emission spectra were used to establish the incorporation of the dye into liposomal formulations. ZnPc into D1 and D2 formulations show a band at 648.5 and 642.5 nm respectively corresponding to dimer ZnPc. The relative fluorescence quantum yields (Φ_F) are 7,2 x 10^{-3} and 8,3 x 10^{-3}, and the singlet oxygen quantum yield production (Φ_Δ) values are 0,34 and 0,42 for D1 and D2 respectively.

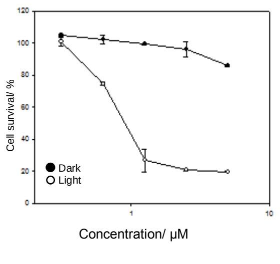
The effect of different concentrations of phthalocyanines on KB cell survival was evaluated in the dark and upon exposure to a light dose of 4.7 J cm^{-2},between 630-700 nm during 40 minutes. No dark cytotoxicity was observed when cells were exposed up to a 100 μg/ mL concentration of liposomes. On the contrary, when cells were treated with ZnPc incorporated into D1 and D2, cell viability diminished in a concentration-dependent manner, the 50% inhibition of cell proliferation (IC_{50}) being obtained at a concentration less than 1 μM.

In conclusion, ZnPc liposomes have a good cytotoxic behavior, despite the fact of the dye dimerization.





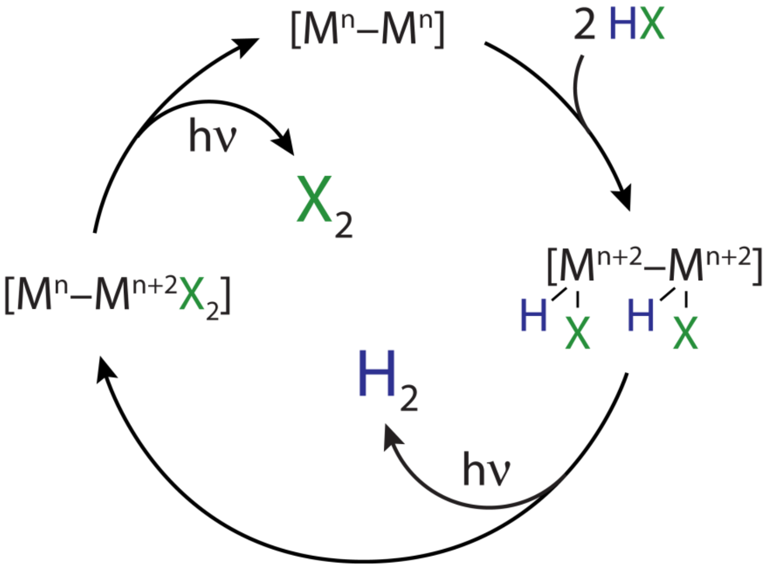




Mechanistic Insights into HX (X = Cl, Br) Splitting Catalysis

Daniel A. Lutterman,[1] **Timothy R. Cook,**[1] **Julien Bonin,**[2] **Thomas S. Teets,**[1] **Daniel G. Nocera**[1]
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, [1] *and Laboratoire d'Electrochimie Moléculaire, Unité Mixte de Recherche Université – CNRS No 7591, Université Paris Diderot, Bâtiment Lavoisier, 15 rue Jean de Baïf, 75205 Paris Cedex 13, France*[2]

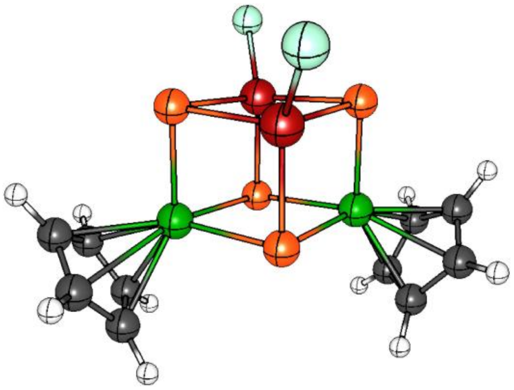
Solar energy may be stored by using it to drive the thermodynamically uphill chemical reaction taking HX (X = Cl, Br) to H_2 and X_2. Facile photocatalytic hydrogen evolution from HX solutions has been previously demonstrated using a phosphazane bridged dirhodium complex, following oxidative addition of two equivalents of HX (illustrated below). However, photoelimination of halogen from the resultant mixed valence complex is hindered by the challenge of activating strong metal-halide (M–X) bonds that are the byproducts of H_2 elimination. In this dirhodium system, the quantum yield for activation of the Rh^{II}–X bond is < 1%. Hence, the overall efficiency for the H_2 photocycle is limited by the efficiency of halogen elimination. A recent advance in M–X bond activation has been realized using a diplatinum(III,III) hexachloride complex that exhibits an unprecedented 38% quantum yield for this activation step. This elevated quantum yield has enabled Pt^{III}–Cl activation to be monitored for the first time on an ultrafast time-scale and development of a mechanistic model. These time–resolved investigations will be discussed here.



Non Linear Optical Properties of the $[(Cp^*M)_2(\mu_3\text{-}S)_4(M'L)_2]^q$ family

Fernando Miranda, Desmond MacLeod Carey and Ramiro Arratia-Pérez
Departamento de Ciencias Químicas, Universidad Andres Bello, Relativistic Molecular Physics (ReMoPh) group, Republica 275, Santiago, Chile

In this work we calculate the electronic structure and non-linear optical properties of a series of molecular clusters, with cubane type structure, titled as $[(Cp^*M)_2(\mu_3\text{-}S)_4(M'L)_2]^q$. (M=green, S=orange, M'=red, L=Ligth Blue) (M=Cr, Mo W, M'L=CuI (1), M'L=NiCO (2); Cp*= a ciclopentadienil ligand). Third order non linear optical properties have been reported (1) for $[(Cp^*Mo)_2(\mu_3\text{-}S)_4(CuI)_2]^{3-}$; For the rest of the complexes of this family, their NLO properties are virtually unknown. In this context, the aim of this work is to present the results that answer the following question:
Is it possible to modify the cubane-like core in $[(Cp^*Mo)_2(\mu_3\text{-}S)_4(CuI)_2]^{3-}$ to change or improve the NLO performance of this cluster family?



References:
1) Z-G. Ren, H-X. Li, G-F. Liu, W-H. Zhang, J-P. Lang, Y. Zhang, Y-L. Song, *Organometallics* **2006**, 25, 4351.
2) M.D. Curtis, P.D. Williams, W.M. Butler, *Inorg. Chem.* **1988**, *27*, 2853.

Acknowledgments:
The authors thanks the financial support of FONDECYT Grants 1100283 and 1110758, and PROJECT MILLENNIUM No. P07-006–F

Synthesis of model sensitizer dyes for efficient hydrogen photoproduction

Ernesto Mariño-Ochoa[1], Ana L. Moore[2], Thomas A. Moore[2], Devens Gust[2], Rodrigo E. Palacios[3], Gonzalo Cosa[4], Jesse J. Bergkamp[2], Benjamin D. Sherman[2], Vicente Arbesú-Lago[1]

[1]*Department of Chemistry, Tecnológico de Monterrey, Campus Monterrey, Monterrey, México*
[2]*Center for Bioenergy and Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, USA*
[3]*Department of Chemistry, Universidad Nacional de Río Cuarto, Río Cuarto, Argentina*
[4]*Department of Chemistry, McGill University, Montréal, Canada*

One of the main challenges humanity is facing in this century is the supply of all the energy requirements. Furthermore, this must be met in a sustainable way to alleviate the impact of the energy industry on global warming. One approach is to take advantage of the abundant solar energy reaching earth. Therefore we need to find a way to convert and store this abundant energy resource efficiently. The sustainable production of hydrogen could be an answer to this problem through the conversion of the solar energy into chemical energy by means of a photoelectrochemical cell. We have shown that a prophyrin-sensitized, Grätzel-based photoelectrode is marginally effective at hydrogen synthesis due to the insufficiently negative potential of the conduction band of TiO2 and the excited state of the porphyrin. This could be overcome by the use of sensitizer dyes with sufficiently low potential excited states and semiconductors with adequate conduction bands. We have synthesized model silicon phthalocyanines with the required potentials and have devised a method to prepare such dyes to be used in a photoelectrochemical cell for the photoproduction of hydrogen.

Modeling photoprotection in Andean plants: deactivation pathways of the excited-states of main flavonoids present in *Zuccagnia punctata* Cav.

Marcela Martin[1,2], **Faustino E. Morán Vieyra**[1], **Claudio D. Borsarelli**[1]
INQUINOA- CONICET. UNSE. Av. Belgrano (S) 1912. G4200ABT, Argentina. [1] *Present address: INIFTA, UNLP. Diagonal 113 y 64 (CP. 1900), Argentina.* [2]

Sunlight irradiance is of major importance for all living organisms, in particular as main source of energy for plants and the majority of bacteria. However, an increment of the input of the sunlight irradiation, especially of the ultraviolet radiation (UV), can affect seriously the cellular systems and compromise the survival of several species. In recent decades, the amount of UV radiation that penetrates the earth's surface has increased from 1% to 3% per year due to the alarmingly weakening of the O_3 layer. Considering that UVA represents >95% of the UV radiation incident on the Earth's surface, in the present work we explore the photophysical and photochemical properties of the flavonoids present in the leaves of the Andean shrub *Z. punctata*: 7-hydroxyflavanone (7HF), 2',4'-dihydroxychalcone (DHC), and 3,7-dihydroxyflavone (DHF) in solution upon UVA excitation in order to characterize the deactivation pathways of their excited states and evaluate their functionality as photoprotective biocompounds.

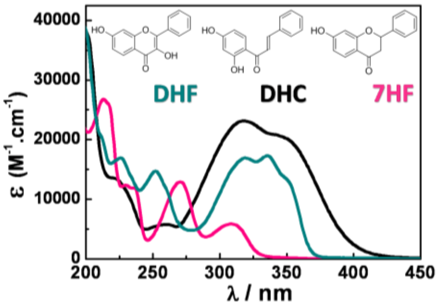


Figure 1: UV-Vis absorption spectra of 7-hydroxyflavanone (HF), 2',4'-dihydroxychalcone (DHC), and 3,7-dihydroxyflavone (DHF) in acetonitrile (ACN), together with their chemical structure.

Flavonoid		**7HF**	**DHF**	**DHC**
p*K*$_a$		6.80 ± 0.02	7.31 ± 0.01	7.36 ± 0.02
Φ^F	**Ethanol**	0.004	0.056	$<10^{-4}$
	Toluene	0.005	0.047	$<10^{-4}$
	Water	0.008	0.014	$<10^{-4}$
	ACN	0.002	0,011	$<10^{-4}$
Φ^r	**Ar / ACN**	n.d.	0.017	0.001
	Air / ACN	n.d.	0.077	0.014
Φ^Δ / ACN		n.d.	0.030	0.027
α	**Ar / ACN**	n.d.	0.956	0.997
	Air / ACN	n.d.	0.897	0.965

Table 1: pK$_a$ values of the first deprotonation equilibrium, fluorescence quantum yields, **Φ^F**, photodegradation quantum yields, **Φ^r**, molecular singlet oxygen quantum yield, **Φ^Δ**, and the fraction of energy absorbed which it is quickly released as heat, **α**, for the studied flavonoids.

Interesting, among theses studied flavonoids, the chalcone DHC showed the highest molar absorption coefficient in the UVA range ($\varepsilon_{320} \approx 20000$ M^{-1}cm^{-1}), and also the lowest quantum yield of photodegradation (≈ 0.1%). Basically, the energy degradation mechanism is through non-radiative processes from the singlet state, since no fluorescence was detected for this compound ($\Phi^F < 10^{-4}$) and the percentage of triplet states formed is not higher than 1%. Also both 7HF and DHF have similar photophysical properties to those observed for DHC, i.e. very low fluorescence and triplet quantum yields (<3%). Another interesting aspect is that these flavonoids has p*K*$_a$ values of the first deprotonation equilibrium close to physiological pH (7.4), increasing the spectral red-shifting , molar absorptivity, and reducing fluorescence quantum yield enhancing its functionality as photoprotective species. The spectral sum of these three main flavonoids of *Z. punctata* overlaps both the UVB and UVA regions, explaining the good UV photo-resistance of the shrub. This photoprotective mechanism of these flavonoides is combined with their antioxidant activity [1].

[1]. F.E. Morán Vieyra, I.C. Zampini, R.M. Ordoñez, M.I. Isla, H.J. Boggetti, V. De Rosso, A.Z. Mercadante, R.M.S. Alvarez, C.D. Borsarelli. *Free Rad. Res.* **43**, 553-564 (2009).

Luminescent Properties of Silicone modified/doped with dyes for Technological Applications

Paulo Alves[1], **Tatiana Martins**[1]
[1]*Federal University of Goiás – UFG,Campus II – Samambaia, Vila Itatiaia, P.O.Box 131, Zip Code: 74001-970, Goiânia, GO, Brazil*

Silicones are a class of inorganic materials that find application in a range of industries, such as textile, electrical, electronic and, lately, in nanotechnology. They have been attracted the researchers attention, specially due to their high flexibility, related to the ease of rotation of Si-O bonds, that achieve angles between 104 and 180º [1,2]. Their mechanical properties can be controlled by cure processes, such as hydrosilylation [3]. It consists of a highly selective reaction that goes under the mechanism proposed by Chalk [3]. By this process, some modification can be processed, as addition of organic compounds to the main chain of the silicone. With the objective of confer luminescent properties to a silicone, organic dyes were covalently attached to polymeric backbone, giving rise to a colored, luminescent, malleable, and chemical and thermal stable hybrid material. These materials were studied by fluorescence spectroscopy techniques and microscopy techniques. Changes in color due to weather and UV radiation exposure were also evaluated aiming at a technological application.

Polysulfone ultrafiltration membranes modified by UV irradiation. Study of Hydrophilicity and Pore Size Increases

Martin Masuelli*[,1], **Ariel Ochoa***, **José Marchese***
*** Laboratorio de Membranas, Instituto de Física Aplicada, CONICET, UNSL. Argentina.**
[1] Cátedra de Química Física II, Área de Química Física. Departamento de Química. Fac. de Química, Bioquímica y Farmacia. UNSL. ***masuelli@unsl.edu.ar***

Introduction. Membrane technology is applied at the treatment of emulsified wastewater from metalworking industry. The oil-wter emulsion is very contaminant, and very difficult to treat. Ultrafiltration is a low-cost treatment and efficient water recovery. Membranes Polysulfone (PSF) with two different pore sizes are irradiated with UV, in order to obtain membranes more hydrophilic and of larger pore size.

Synthesis. PSf (Udel 3500P) 17 and 20% wt. were dissolved in N,N-Dimthylformamide (Sigma), next mixed with 10% polyethylene glycol (35kDa, Stanton). Finally, dissolved were casting in support (FO2430, Fraudemberg) and coagulated in water at 25ºC.

UV-Irradiation**.** Were prepared heterogeneous solution that contain: 5g membrane of 374 cm^2, and one litter of ethanol (98% in vol.), previously degassed with N_2. Heterogeneous solution was introduced in glass recipient of 25x15cm. The membranes were irradiated to 25ºC with irradiation lamp (MineralLightUVSL-58 of 220V, 50Hz, 12A). The irradiation time was 1, 2, and 4hs. Then irradiation, membranes were washed with water for 24 hs.

Characterization. The membranes were analysed by contact angle (θ), retention solute permeation (r_p), fouling test (emulsion Tutela K2P oil solution 10%, COD 52000ppm O_2), and hydraulic permeability (L_h) (Minitan S cell and Millipore peristaltic pump). The subscript “i” is referring to initial and “ii” after irradiation.

Membrane	θ	L_{hi}x10^9	L_{hii}x10^9	r_{pi} (nm)	r_{pii} (nm)	COD
20PSf	79.2	0.97	-	2.11	-	230
20PSf1UV	78.3	1.29	5.23	2.23	10.23	550
20PSf2UV	77.4	1.36	4.45	2.34	10.56	430
20PSf4UV	77.0	1.43	4.56	2.55	11.78	535
17PSf	79.0	1.29	-	11.10	-	520
17PSf1UV	77.8	1.09	3.35	11.00	34.23	588
17PSf2UV	76.6	1.71	3.99	12.33	36.44	623
17PSf4UV	76.1	1.85	5.39	12.56	37.58	696

Discussion. The increment on contained of PSf on solution of casting decreased of pore size. Radii pore distribution (see table) evidence an increment of mean pore size of irradiated membranes respect to 20PSf and 17PSf. Hydraulic permeability for no modified membranes (17PSf 1.29x10^{-9}, 20PSf10 0.97x10^{-9} m/s Pa) was more low what irradiated membranes from one order magnitud. Contac angle for PSf was 79 degree, but irradiated membranes were lower (due to major irradiation time). The fouling test shows that membranes were crossed with a small portion of the emulsion and showing a COD more high to pore size height.

Conclusion. Irradiated membranes (IM) present low hydrophilicity and high hydraulic permeability. Irradiation proceeding drive rupture of bond via free radicals, generated pore greater and group affinity of water so –COOH, -OH. The irradiation influence is about pore size increment that a major hydrophilicity. The exclusion in fouling is by particle size. The IM presented high fouling and COD by inreased pore size.

References. Nystrom, M., Jarvinen, P. (1991). Modification of polysulfone ultrafiltration membranes with UV irradiation and hydrophilicity increasing agents. Journal of Membrane Science 60, 275-296.

Experimental and Computational Studies of Porphyrin and Naphthalocyanine Dyes as Sensitizers in Artificial Photosynthetic Water Splitting Cells.

Dalvin Méndez-Hernández, Ana L. Moore and Vladimiro Mujica
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, USA

Greenhouse gas emissions generated by the use of fossil fuels presents a variety of ecological, climatic and economic threats to society. Thus, research into renewable energy has become a priority. Among all renewable energy options, solar energy is an attractive choice because the sun irradiates more energy on the earth's surface in one hour than the total amount that humans currently consume in one year. Unfortunately, solar irradiation is intermittent and therefore energy from the sun would need to be stored in chemical bonds (e.g. hydrogen gas, methane) so it can be used when required. Inspired by the natural process of photosynthesis, 10,20-bis(pentafluorophenyl)porphyrins (PF_{10}) and silicon octabutoxy-naphthalocyanines ($Si(OBu)_8Nc$) will be used to drive water oxidation and hydrogen production processes, respectively. A series of these dyes have been synthesized and characterized. When attached to SnO_2, and upon excitation with light, PF_{10} will inject electrons into the conduction band of the semiconductor, thereby generating the oxidized porphyrin radical cation. The potential of this radical cation will drive the oxidation of water by a water oxidation catalyst coupled to the porphyrin. The hydrogen production process will be driven by the solar energy adsorbed by $Si(OBu)_8Nc$ dyes anchored to TiO_2 and coupled to a catalyst for proton reduction. To attach the dyes to their respective semiconductor electrode, phosphonate anchoring groups are desired, and will be used, because the carboxylate anchoring groups, normally used in dye-sensitized solar cells, are known to be unstable in aqueous environments. Density Functional Theory is being used to predict and understand the electronic and spectroscopic properties of the dyes under study and evaluate their potential for use in photo-electrochemical cells.

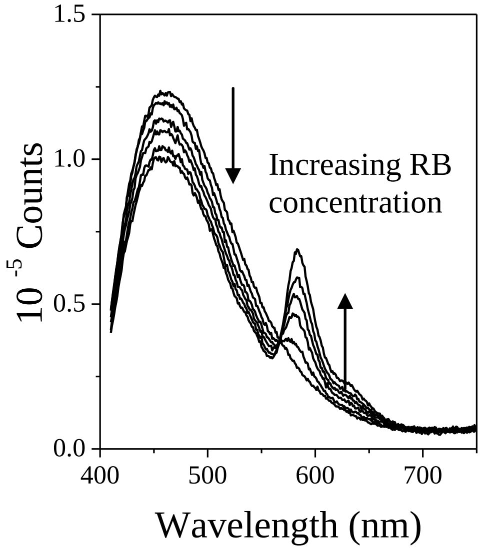
Solvent-Solute Excitation Energy Transfer between 1-Butyl- 3-Methylimidazlium Chloride Ionic Liquid and Rose Bengal

Martín Mirenda[1] **and Karin Gutkowski**[1, 2]
[1] CNEA- CAC- Gerencia de Química, Av. Gral. Paz 1499, 1650 San Martín, Pcia. de Buenos Aires, Argentina. [2] Member of Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET.

We study the solvent-solute excitation energy transfer phenomenon between the Ionic Liquid (IL) 1-butyl-3-methylimidazolum chloride, [bmim][Cl], and Rose Bengal (RB). Absorption, steady-state fluorescence measurements, and anisotropy calculations were performed on RB-IL solutions for different RB concentrations.

Absorption measurements of the RB-[bmim][Cl] show a characteristic RB band with no evidence of RB aggregation nor solvent-solute associations. The RB does not absorb in the blue region.

Fluorescence spectrum of pure [bmim][Cl], recorded at λ_{exc} = 400 nm shows an emission maximum in 470 nm. When the dye is added to the system, the fluorescence intensity of the IL decreases while a characteristic RB emission band appears, showing a clear isostilbic point in 560 nm (figure on the right).



The presence of RB fluorescence when only the IL is excited is indicative of a solvent-solute energy transfer process. The calculated efficiencies for the total excitation energy transfer and the non-radiative excitation energy transfer, show that the non-radiative mechanism dominates at low RB concentration (diffusional events in the system are totally discarded due to the high viscosity of the IL at room-temperature).

Steady-state emission anisotropy spectra were calculated for the pure [bmim][Cl] and for the [bmim][Cl]-RB system with the aim to explain the mechanism involved in the observed energy transfer process. The solutions were excited at two different wavelengths so the dye or the IL is irradiated selectively. The experiments reveal that the solvent-solute energy transfer phenomenon is mediated by excitation energy migration trough different IL domains.

Gum Arabic Interaction with Excited States of Riboflavin and Reactive Oxygen Species

Laura Boiero[1], Susana Criado[2], Lorena Valle[3], Mariana A. Montenegro[4], Norman García[2], and Claudio D. Borsarelli[3]

[1]*Departamento de Química, Facultad Regional Villa María, Universidad Tecnológica Nacional, Av. Universidad 450, Villa María, Córdoba, Argentina.*

[2]*Departamento de Química, Universidad Nacional de Río Cuarto, Campus Universitario, Río Cuarto, Córdoba, Argentina.*

[3]*Instituto de Química del Noroeste Argentino (INQUINOA-CONICET), Universidad Nacional de Santiago del Estero, Av. Belgrano 1912, Santiago del Estero, Argentina.*

Gum arabic (GA) is the exudates obtained from acacia trees, *Acacia senegal* and *Acacia seyal*, which grows mainly in Sudan, Africa. Structural studies showed that GA is a group of macromolecules characterized by a high proportion of carbohydrates (97%) and low proportion of protein (1-3%). In biological milieu, GA plays antioxidant activities, influences on lipid metabolism, and contributes positively on kidney, cardiovascular, and gastrointestinal diseases. On the other hand riboflavin (Rf) is present in many biological systems and can act as a photosensitizer to generate reactive oxygen species (ROS) producing photoinduced damage or photo-oxidation of biological molecular targets.

In this work, we studied the antioxidant capacity of GA towards ROS generated chemically and by Rf photosensitization. In particular, we analyzed the GA interaction with the triplet excited state of Rf, ^{3}RF, and ROS such as superoxide anion radical, $O_2^{\bullet-}$, hydroxyl radical, $^{\bullet}$OH, and singlet molecular oxygen, $^1O_2$.

Laser flash photolysis experiments were performed using a laser pulse excitation at 355 nm to generate the ^{3}RF, with transient absorption at 720 nm. ^{3}Rf was efficiently quenched by GA, with a rate quenching constant $k_q^{RF\text{-}GA} = 1.6\times10^9$ M^{-1}s^{-1}. Additionally, the total quenching and reactive rate constant of $^1O_2$ by GA, i.e. $k_{t,\Delta} = 2.7 \times 10^7$ M^{-1}s^{-1} and $k_{r,\Delta} = 7.6 \times 10^4$ M^{-1}s^{-1}, respectively were obtained by actinometry, and indicated that GA is a good catalytic (physical) quencher of $^1O_2$.

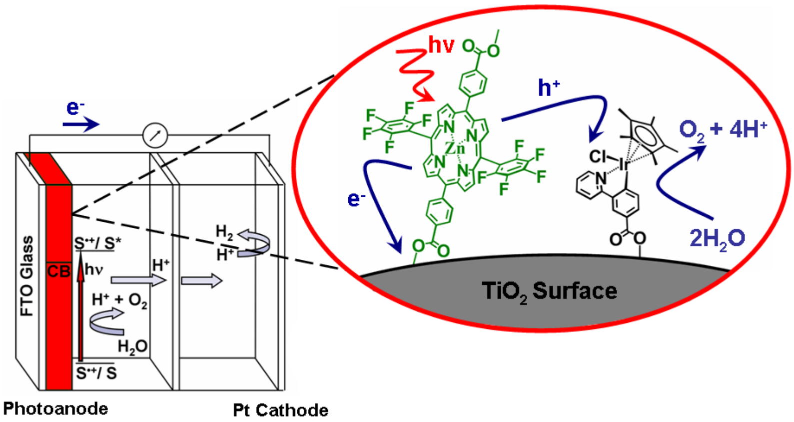
Finally, the GA ability to scavenging both $^{\bullet}$OH and, $O_2^{\bullet-}$ was investigated. The Fenton reaction was used to generate $^{\bullet}$OH and detected by UV-Vis spectroscopy at 532 nm due to formation of an adduct between malonaldehyde with thiobarbituric acid. The $O_2^{\bullet-}$ scavenging ability determination was based on GA ability to inhibit the Monoformazan (MF$^+$) formation (λ_{max} = 530 nm) by reducing Nitrotetrazolium Blue (NBT^{2+}). In both cases, the GA inhibition percentage using Trolox as reference antioxidant, yielded Trolox Equivalent Antioxidant Capacity (TEAC) values of 0.71 and 1.82 for deactivation of $^{\bullet}$OH and $O_2^{\bullet-}$ respectively.

The present results show that GA may act as an effective antioxidant, particularly in Rf photo-sensitized processes, since prevent the formation of ROS species by quenching of ^{3}RF, and also deactivates ROS ($^1O_2$ and $O_2^{\bullet-}$) efficiently. This antioxidant functionality is associated with the small protein moiety of GA by the action of the amino acid residues such as histidine, tyrosine, and proline.

Bioinspired Approaches to Solar Fuels

<u>Gary F. Moore</u>, James D. Blakemore, Rebecca L. Milot, Jonathan F. Hull, Hee-eun Song, Lawrence Cai, Victor S. Batista,* Charles A. Schmuttenmaer,* Robert H. Crabtree,* and Gary W. Brudvig*
Yale University, Department of Chemistry, New Haven, CT 06520-8107, USA

Artificial photosynthesis is a long-sought goal in solar energy research. By splitting water into O_2 and a fuel such as H_2, two problems are addressed: energy storage and the production of a potential transport fuel. Practical application of this integrated approach will ultimately require effective coupling of light capture, photochemical charge separation and efficient catalysis. A challenging feature is the coupling of single-electron photochemical events to multi-electron catalytic reactions. We have prepared a water-splitting photocell that uses a specially designed photoanode to which are attached both a high-potential zinc porphyrin dye for light absorption and a homogeneous iridium catalyst for water oxidation. The cell is completed by a standard Pt cathode for H^+ reduction. The porphyrin sensitizers effectively extend light absorption by the anode well into the visible region and the photoexcited dye injects electrons into the conduction band of TiO_2 nanoparticles. Electrochemical measurements confirm that the photooxidized dye is energetically capable of water oxidation and that immobilized catalysts remain active on the surface. Thus, the photoanode optically resembles the porphyrin yet electrochemically responds like the catalyst when it is immersed in aqueous solutions. Photoelectrochemical data show that illumination of the codeposited anode in water results in a marked enhancement and stability of the photocurrent, providing evidence for light-induced activation of the catalyst. Further optimization of the light absorber, catalytic unit and linker interface to the semiconductor surface is in progress.



PHOTODEGRADATION OF MALACHITE GREEN IN THE PRESENCE OF TiO_2 ON A FLAT PLATE REACTOR

Marlene Morales, Aline Donaire, Oscar Waissbluth, Fernando León, Fernando Henríquez.
Department of Chemistry, Universidad de Tarapacá, Velásquez 1775, Arica, Chile.
mmorales@uta.cl

The photodegradation of triphenylmethane dye malachite green (MG) was studied using the heterogeneous photocatalysis process. We used a flat plate photoreactor, using as catalyst titanium dioxide The main parameters in the degradation of MG were studied and optimized. The optimal conditions for the degradation of MG solution were the mass of malachite green, a mass of titanium dioxide, pH, solution flow, addition of salts and the intensity of radiation, spectrophotometric measurements were made, potentiometric and determination of the Reynolds number (flow).

Complete degradation of MG (> 99%) was achieved after 150 minutes of solar irradiation under optimized conditions of the ratio of 0.04 grams of titanium dioxide per milligram of MG , pH = 7 and the system flow is turbulent.

The effect of added Cl, NO_3^- and SO_4^{2-} anions on the degradation kinetics was also studied. Sulfate anion did not inhibit the degradation of MG, while chloride, nitrate anion reduce the disappearance of MG.

Keywords: heterogeneous photocatalysis, malachite green. titanium dioxide.

Comparison of two different expressions of the kinetic equation for a photocatalytic reaction

Guadalupe B. Ortiz de la Plata[1], Orlando M. Alfano[1], Alberto E. Cassano[1] , Francesco Santarelli[2], Giovanni Camera-Roda[2]
INTEC (Universidad Nacional del Litoral - CONICET) Colectora de Ruta Nacional Nº 168, Km. 472,5 - 3000 Santa Fe, Argentina[1];
DICMA (Università di Bologna) Via Terracini 28 - 40131 Bologna, Italy[2]

Considering that the initial step of a photocatalytic reaction is the absorption of the photons, for a photocatalytic process the local rate of the reaction is strongly affected by the photon flux in that point of the reactor. Unfortunately not all the absorbed photons are effectively utilized for the reaction and, as a consequence, the quantum yield is typically low. Furthermore it has been experimentally observed and, under some assumptions, it has been theoretically demonstrated that the higher is the rate of absorption of photons the lower is the quantum yield. This phenomenon complicates the analysis and the design of photocatalytic reactors since, when the quantum yield is not constant, it becomes necessary to get a detailed appraisal of the photon flux, that is of the intensity of the radiation, inside the reactor. Actually in a photocatalytic reactor the intensity of the radiation varies very much not only with the position but also with the direction due to absorption and scattering. It must be observed that it is almost impossible to acquire experimentally the intensity distribution, so it is a common practice to obtain it by numerically solving the integro-differential equation which expresses the radiant energy balance. Then from the knowledge of the values of the intensities in a point coming from all the directions the LVREA (local volumetric rate of radiant energy absorption), or equivalently the LVRPA (local volumetric rate of photon absorption), can be estimated through the relationship: LVREA= $\int_{4\pi} \kappa \, I \, d\Omega$ where κ is the absorption coefficient, so that the integration considers the intensities on all the solid angle.

Generally the constitutive equation for the rate of reaction, $\mathcal{R}$, assumes an order, α, of reaction with respect to the LVREA which possibly can vary between 0 and 1 according to the value of the intensity of the radiation. By following this approach $\mathcal{R} \propto \mathrm{LVREA}^{\alpha}$. However, from a theoretical point of view, it would be more rigorous to assume that $\mathcal{R} \propto \int_{4\pi} \kappa \, I^{\alpha} \, d\Omega$. Bearing in mind that the intensities in a given point may vary very much with the direction, it is obvious that $\int_{4\pi} \kappa \, I^{\alpha} \, d\Omega \neq \left(\int_{4\pi} \kappa \, I \, d\Omega \right)^{\alpha}$ whenever $\alpha \neq 1$. In the present work the consequence of using the approximate expression of the constitutive equation of the rate of reaction in substitution of the more rigorous one are examined for an annular photocatalytic reactor at different values of all the intervening parameters. Some rules are derived which establish the conditions for which the substitution gives negligible errors.

3st Poster session

Friday May 20

PLASMONIC EFFECTS OF GOLD NANOPARTICLES ON THE PHOTOCHEMISTRY OF METHYLENE BLUE

Natalia L. Pacioni, Maria González-Béjar, Emilio Alarcón, Katherine L. McGilvray and Juan C. Scaiano
*Centre for Catalysis Research and Innovation (CCRI), Department of Chemistry,
University of Ottawa, 10 Marie Curie, Ottawa, ON, K1N 6N5, Canada.*

Nowadays, the interaction of light with metallic nanoparticles, either in a direct or indirect way, plays a key role in most of the physical and chemical phenomena that are studied with nanomaterials, from their synthesis to their various applications. For instance, photophysical properties of a molecule in the proximity of a metal nanoparticle surface could be modified to some extent by Surface Plasmon interactions undergoing transmitter/antenna effects.[1,2] Generally, these interactions have been explored in the ground and singlet excited state, where either quenching or enhancement of fluorescence has been observed.[3]

Here, we present the plasmonic effects of aqueous gold nanoparticles ~15 nm (AuNP) on methylene blue triplet excited states (^{3}MB*) upon 650 nm laser excitation.[4] Furthermore, NIR luminescence studies have been also performed and a decrease in the singlet oxygen quantum yield of MB was observed when AuNP are present. Finally, the effects on the antenna phenomena by in situ laser-mediated shape and size modification of larger AuNP 50-70 nm will be discussed.

[1] Anger, P.; Bharadwaj, P.; Novotny, L., *Phys Rev. Lett.* **2006**, 96, 4.
[2] Bharadwaj, P.; Novotny, L., *Opt. Express* **2007**, 15, 14266.
[3] Lakowicz, J. R., Principles of Fluorescence Spectroscopy, 3rd Ed. Springer, **2006**.
[4] Pacioni, N.L.; González-Béjar, M.; Alarcón, E.; McGilvray, K.L.; Scaiano, J.C., *J. Am. Chem. Soc.* **2010**, 132, 6298.

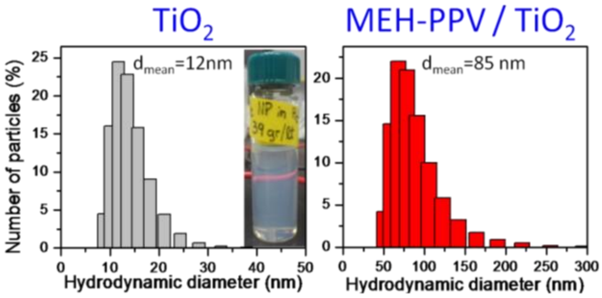
HYBRID POLYMER/SEMICONDUCTOR NANOPARTICLES: SYNTHESIS AND CHARACTERIZATION

Laura Hernandez[1], Romina Gramaglia[1], Sonia Bertolotti[1], Carlos Chesta[1], Robert Godin[2], Gonzalo Cosa[2], Rodrigo Palacios[1]
[1] Dpto. Química, Universidad Nacional de Río Cuarto, Río Cuarto, Argentina
[2] Dept. Chemistry, McGill University, 801 Sherbrooke St. W., Montréal, Canada
rpalacios@exa.unrc.edu.ar

Hybrid Photovoltaic devices (PV) based on conjugated polymers and inorganic semiconductors are of great interest because they allow the production of low-cost, large area and flexible solar cells [1] by combining the unique properties of inorganic semiconductors and conjugated polymers. However, the inherent incompatibility between these materials generally causes macroscopic phase separation and poor electrical contact limiting the PV efficiency. Therefore the synthesis and characterization of nanostructured materials containing conjugated polymers and inorganic semiconductors with good electrical contact is highly desirable. Herein we describe the synthesis and characterization of hybrid nanoparticles (NPs) containing a commercial conjugated polymer (poly [2-methoxy-5-(2-ethyl-hexiloxi)-P-phenylene vinylene] ; MEH-PPV) and titanium oxide (TiO_2) inorganic semiconductor.

TiO_2 NPs were synthesized using modified sol-gel procedures[2] obtaining aqueous suspensions of small (d = 12 nm) NPs with excellent poly-dispersity (PDI = 0.160), high concentration (50 g/l) and excellent optical quality. Hybrid (MEH-PPV/TiO_2) and polymer only (MEH-PPV) nanoparticles were formed by a controlled precipitation method [3] producing particles of $25<d<90$nm and $0.11<PDI<0,17$ depending on the precipitation conditions. A comparative study of stationary and time-resolved fluorescence in solution indicates that fluorescence is quenched in hybrid NPs compared to polymer only NPs, the magnitude of quenching increases with increasing amount of TiO_2.

Analysis of the energy levels in these nanoparticle systems indicates that the observed fluorescence quenching is due to photoinduced electron transfer from the polymer into the metal oxide conduction band. A comparative study of the emission and excitation spectra in hybrid NPs and MEH-PPV indicates that excitation energy is efficiently funnelled to "special" low energy chromophores which are responsible for most of the photoemission in these systems. The hybrid NPs represented herein are useful models to study electron and energy transfer in nanostructured donor-acceptor systems and are currently being studied by single molecule fluorescence spectroscopy techniques.



References

1- S. Gunes, H. Neugebauer, N.S. Sariciftci,*Chem. Rev.*107, 1324, **2007**.

2- a) T. Bell, C. Pagba, M. Myahkostupov, J. Hofkens, P. Piotrowiak, *J. Phys. Chem. B* 110, 25314, **2006**. b) I. Martini, J. H. Hodak, G. V. Hartland, *J. Phys. Chem. B* 103, 9104, **1999**.

3- Palacios R.E., Fan F-R.F., Bard A.J., Barbara P.F. *Nat Mat*, 6, 680-685, **2007**.

Excited-State Physical Properties of Aromatic Heterocycles and Related Compounds – an Overview

Cyril Párkányi,[1] **Jean-Jacques Aaron**[2]
[1]*Department of Chemistry and Biochemistry, Florida Atlantic University, 777 Glades Road, P.O. Box 3091, Boca Raton, FL 33431-0991, USA; parkanyi@fau.edu*
[2]*Laboratoire ITODYS, associé au CNRS UMR 7086, Université Paris Diderot – Paris 7, 15, rue Jean de Baïf, F-75205 Paris Cédex 13, France; jeanjacquesaaron@yahoo.fr*

For a number of years, we have been interested in excited-state physical properties of aromatic heterocycles and related compounds and their comparison with the corresponding ground-state properties, with a special attention paid to biologically active compounds. Examples of the physical properties include, but are not limited to, electronic absorption and emission (fluorescence, phosphorescence) spectra, dissociation/ionization constants, and ground- and excited-state dipole moments. The compounds under study included pyridines, quinolines and isoquinolines, substituted indoles, aromatic and heteroaromatic triazenes, fused furans, coumarins, pyrimidines and purines, acridines, pteridines, phenazines and phenothiazines, thiazoles, fused thiophenes, thienofurans, and various aromatic dyes. In addition to experimental results, theoretical calculations were carried out in many cases. Examples of the studies representing various excited-state properties will be provided.

Riboflavin-induced photodegradation of tryptophan in sodium sulfosuccinate (AOT)-*iso*-octane-water

Hugo A. Perez, Faustino E. Morán Vieyra, Lorena Valle and Claudio D. Borsarelli.
Instituto de Química del Noroeste Argentino (INQUINOA-CONICET), Facultad de Agronomía y Agroindustrias, Universidad Nacional de Santiago del Estero, Av. Belgrano 1912, Santiago del Estero, Argentina.

Flavins play an important role in photosensitized reactions that include a wide range of electron donor substrates, such as amino acids. In aqueous solutions, triplet state of flavins reacts with amino acids such as Cys, Trp and Tyr with bimolecular quenching constants between $1\text{-}10\times10^9$ M^{-1} s^{-1} [1]. In aerobic conditions, the flavin photosensitized oxidation of aminoacids was attributed to H_2O_2 produced by dismutation of $O_2^{\bullet-}$, generated by the interaction of O_2 with the triplet of the flavins and/or radical species formed by flavin triplet reaction with the aminoacids [2,3].

However, to our knowledge, there are few studies about flavin-photosensitized oxidation of amino acid in microenvironments which mimic biological system compartmentalization. In this work we study the riboflavin (Rf)-mediated reaction of tryptophan in nanodroplets made of sodium sulfosuccinate (AOT)-*iso*-octane-water by continuous blue-LED (460 nm) and laser pulsed (355 nm) photolysis, using both stationary and dynamic absorption and emission spectroscopies.

The absorption and emission spectra of Rf and Trp indicated that both molecules are located in the inner water-surfactant interface of the reverse micelles. The fluorescence quenching of Rf by Trp is a mixing of static (Perrin) and dynamic mechanism. With the increment of the water content in the reversed micelles (W = $[H_2O]/[AOT]$) the fraction of static quenching is reduced while the dynamic component increases. These results are in agreement with the larger micelar size and fluidity as W increased. The UV-Vis absorption and fluorescence spectra showed the riboflavin conversion to lumichrome and the photoproducts of the indole-flavin type. The rate of formation of photoproducts, measured with the absorbance increment at 320nm was proportional with the increment of the quenching rate constant of ^{3}Rf* by Trp, e.g. k_Q^T= 2.6×10^7, $6.1\times10^7$and 3.3×10^9 $M^{-1}s^{-1}$, for W =3, W= 20 and phosphate buffer solution, respectively, indicating that the photodegradation reaction is mainly govern by triplet state photochemistry. In reverse micelles the product formation is almost six-times lower that in bulk buffer solution. This indicates that the much rigid micellar environment reduces the Rf-mediated transformation of Trp.

---

[1] A. M. Edwards. General properties of flavins in Flavins: photochemistry and photobiology (Ed. E. Silva and A. M. Edwards), Comprehensive series in Photochemical and Photobiological Science, Vol 6, Royal Soc. Chemistry, UK, Chapter 2, pp 13 – 40 (2006).

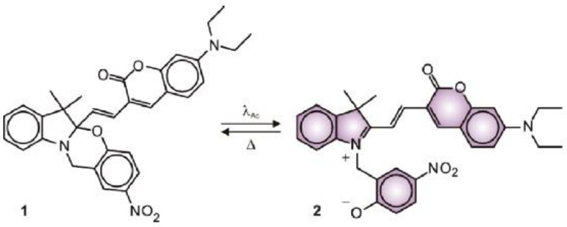
[2] L. Chang- Yuan, L. Yan- Yun. Electron transfer oxidation of tryptophan and tyrosine by triplet states and oxidized radicals of flavin sensitizers: a laser flash photolysis study. *Biochim. Biophys. Acta*. 1571, 71 – 76 (2002).

[3] H. Gorner. Oxygen uptake after electrón transfer from amines, amino acids and ascorbic acid to triplet flavins in air – saturated aqueous solution. *J. Photochem. Photobiol. B*. 87, 73 – 80 (2007).

Fluorescence Switching of a Photochromic Oxazine at the Single-Molecule Level

Marco Petriella,[1] **Erhan Deniz,[2] Salvatore Sortino,[3]**
Mariano L. Bossi[1] and Françisco M. Raymo[2]
[1.] INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires. Pabellón 2, Ciudad Universitaria, 1428 - Buenos Aires, Argentina; [2.] Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, Florida, 33146-0431, United States; [3.] Dipartimento di Scienze Chimiche, Università di Catania, viale Andrea Doria 8, Catania, I-95125, Italy

Photochromic compounds have the ability to switch reversibly between two states with distinct physical properties, under the influence of optical stimulations. This transformation has been exploited to modulate a fluorescence signal in molecular constructs, typically by pairing covalently a fluorophore and a photochrome. In this way, the interconversion of the latter can be invoked to regulate the emission intensity of the former, on the basis of excited-state electron or energy transfer. Alternatively, we have devised a general strategy for fluorescence modulation solely based on ground-state interactions; the photoinduced bathochromic shift of the absorption wavelength of a fluorescent chromophore is produced by an appended photochromic auxochrome. In the present work, we present a fluorescent molecular switch, designed around this mechanism, and the study of its photochemical and photophysical properties, in solution and at the single molecule level.



Compound (**1**), incorporating a fluorescent coumarin and photochromic [1,3]-oxazine[1] within the same covalent skeleton, was prepared in a single step from known precursors in a yield of 40%.[2] The photochemical properties of compound **1** were first investigated in MeCN solutions. Upon excitation at 355 nm the [1,3]oxazine ring opens with a quantum yield of 0.02 to generate the zwitterionic isomer **2**. The latter absorbs at 570 nm and has an emission centered at 645 nm. The process is fully reversible, and the photogenerated isomer **2** reverts to the original state with a lifetime of 0.2 μs. Then, solutions of compound **1** or mixtures of the two isomers were casted onto glass cover slips at low concentration to ensure a sparse two dimensional distribution of dyes. The films were observed in an epifluorescence wide-field microscope to study the switching and emission properties at the single-molecule level. Excitation was performed at 532 nm, where only the open isomer absorbs, and detection was recorded in an EM-CCD camera. Typically, 2000 frames were obtained for a total time of ~1 second (depending on the frame time). The images were then analyzed with a self-written software to extract time-traces and position of hundreds of single molecules simultaneously, and to analyze the switching behavior of dyad **1**. Similar experiments were performed with a model compound containing the same fluorophore but lacking the switching ability, to asses the influence of the triplet state in the blinking behavior.

1. M. Tomasulo, S. Sortino and F. M. Raymo; *Org. Lett.* 2005, **7**, 1109-1112
2. E. Deniz, S. Sortino and F. M. Raymo; *J. Phys. Chem. Lett.* 2010, **1**, 3506–3509

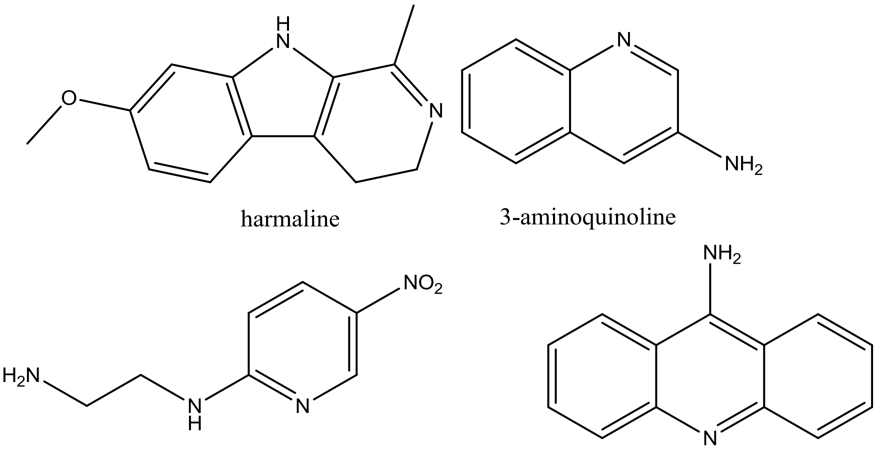
Photoacoustic and luminescence characterization of heterocyclic aromatic basic UV-MALDI matrices

<u>Gabriela Petroselli</u> and Rosa Erra-Balsells
[1] *CIHIDECAR-CONICET, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, 3 Ciudad Universitaria, (1428) Buenos Aires, Argentina.*
Pedro David Gara and Gabriel M. Bilmes
Centro de Investigaciones Ópticas-CIOp (CONICET-CIC) and Universidad Nacional de La Plata, Casilla de Correo 124, (1900) La Plata, Argentina

Ultraviolet Matrix-assisted laser desorption/ionization (UV-MALDI) is a method based on dispersing a macromolecule (analyte) in a large excess of a matrix (photosensitizer), both in solid sate. The solid mixture is irradiated with a laser pulse and vaporizes. Analyte gas ions are formed and then detected by mass spectrometry (MS). The mechanism of ionization during MALDI is still poorly understood and no adequate quantitative model for the complete process exists. The UV-MALDI technique involves both laser ablation and ionization of the matrix/analyte mixture after electronic excitation of the matrix.

The knowledge of the thermal deactivation process of common UV-MALDI matrices should play a critical role in understanding why some matrices lead more abundant post-source decay as well as prompt decay of the analyte. Furthermore, it will be helpful in order to choose the proper matrix to optimize UV-MALDI-MS analysis.

In this work we studied a group of recently proposed matrices used in UV-MALDI-MS for lipids analysis. The photophysical, photochemical and spectroscopic behaviour of: 9-aminoacridine (9AA), 3-aminoquinoline (3AQ), 2-(2-aminoethylamino)-5-nitropyridine (AAN) and 3,4-dihydro-7-methoxy-1-methyl-9H-pyrido[3,4b]indole (harmaline, Hla) were characterized in acetonitrile and methanol solutions. We studied the photostability of those molecules; their absorption and emission properties in steady-state conditions; its singlet oxygen production by means of time resolved phosphorescence detection, and the calorimetric behaviour and triplet state properties by using photoacoustics measurements.



harmaline 3-aminoquinoline

2-(2-aminoethylamino)-5-nitropyridine 9-aminoacridine

Fig. 1: Molecular structures of the UV-MALDI matrices studied.

Degradation of chlorophenols using TiO_2, in μm and nm size scale, as Heterogeneous Photocatalysis in aqueous suspension. An extended kinetic study in competitive experiments.

Eduardo Pino, Maria Victoria Encinas
Universidad de Santiago de Chile, Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Santiago, Chile, Av. Libertador Bernardo O'Higgins 3363, Estación Central. eduardo.pino@usach.cl

keywords: photocatalysis heterogeneous, chlorophenols, competitive degradation, simulate solar light.

Actually, the treatment of wastewater and the remediation of contaminated water have been an important target of basic and apply science. In this way, applications to environmental cleanup have been one of the most active areas in the heterogeneous photocatalysis, where the most used semiconductor had been the titanium oxide (TiO_2). However, the majority of these studies target to the degradation of only one organic molecule. Only in the last few years, families of organic compound have been studied, but only few studies have been made with mixture of contaminants or complex matrixes[2]. The presence of the different additives could affect the essential process involved in the degradation of a particular contaminant in wastewater[1].

In this work we evaluated the degradation of the *4-chlorophenol* (4-CP) and the *2,6-dichlorophenol* (2,6-DCP), free and in equimolar mixture. Also, we have evaluate the effect of 2,6-DCP (10^{-4} M) in the degradation of different concentrations of 4-CP in aqueous suspension using TiO_2 as heterogeneous photocatalytic, between 2 μm and P25 nanosize scale at constant loading (0.5 gL^{-1}). The initial degradation rate was monitored using High Performance Liquid Chromatography (HPLC). These studies showed that the degradation rate decreases when the CPs concentration was increased separately and in the mixture, suggesting a complex degradation kinetics. The comparison between the degradation of 4-CP and 2,6-DCP separately using TiO_2 around 2 μm and P25 nanosize scale showed that the degradation rate of 2,6-DCP was faster than that of 4-CP in the limit of low concentration (10^{-5} M), but the degradation rate get similar at the high limit concentration (10^{-4} M). On other hand, the results obtained when a mixture of both studied phenols showed that a fast degradation of 2,6-DCP with respect to the 4CP. These results agree with the pKa values of 9.0 and 6.75 reported for 4-CP and 2,6- DCP, respectively. Furthermore, at high concentration limit ($\sim 10^{-4}$M), the kinetic profiles obtained for both semiconductor particles showed the accumulation of two principal products, which were eliminated at long degradation times. This behavior was not observed at low concentration of CPs. In all cases, we observed a decrease of the pH solution; which agree with the HCl generation.[3]

In conclusion our results evidence that the degradation process induced by Heterogeneous Photocatalysis, using TiO_2 and UV or simulated solar light, of mixture is more complex than the degradation of individual *chlorophenols.* Wherefore, studies of competitive degradation must be carrying out with the purpose to obtain a more realistic perspective.

References. [1]*Chem. Rev.* 1995, 95, 69; [2]App. Cat. B. Environm. 1999, 21, 1; [3]J. Photochem. Photobiol. A. Chem. 2008, 200,421

Acknowledgment. Financial support from the Bicentenary of Science and Technology Program, PDA-03, and DICYT-USACH 021141PL are gratefully acknowledged.

Abatement of methidathion from aqueous solutions using TiO_2 pillared magadiite layered silicate as photocatalysts

Cléo T. G. V. M. T. Pires,[1] **Maria L. Marín**,[2] **Miguel A. Miranda**,[2] , **Claudio Airoldi.**[1]
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, São Paulo, Brazil,[1] *Instituto de Tecnología Química-Departamento de Química (UPV-CSIC), Avda de los Naranjos s/n, E-46022 Valencia, Spain*[2]

Degradation of methidathion pesticide has been studied using organic photocatalysts, namely 2,4,6-triphenylpyrylium (TPP) and 2,4,6-triphenylthiapyrylium (TPTP) in homogeneous route and also immobilized inside the pores TiO_2 pillared magadiite. Experiments carried out using a photoreactor showed that methidathion was more easily photo-oxidised by TPTP than TPP despite if homogeneous or heterogeneous media. In the case of TPTP, the hybrid sample with Pi-[Ti]Mag exhibited a better performance than the pure one. Emission spectra impregnated TPP and TPTP materials are showed at Figure 1A. TPP containing samples, curves a, b and d, were excited at 370 nm and emit between 490 and 495 nm, changing considerably the intensity, at relatively agreement with the amounts used, considering the dyes distribution and aggregation uniformity at the inorganic matrix and is also related with surface area and pores ordering. Samples containing TPTP, curves c and e, were excited at 400 nm and emit at 510 and 525 nm, varying the intensity less than TPP samples, but also in agreement with the amounts used and the inorganic matrix surface area.

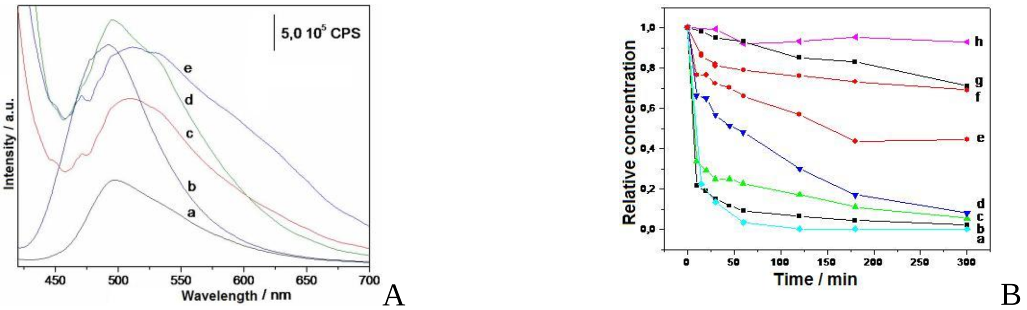


Figure 1. A) Emission spectras of: a) TPP-Pi-[Al]Mag, b) TPP-Silica gel, c) TPTP-Pi-[Al]Mag, d) TPP-Pi-[Ti]Mag and e) TPTP-Pi-[Ti]Mag; B) Photodegradation kinetics with catalysts: a) TiO_2 degussa, P25, b) TPTP-Pi-[Ti]Mag, c) TPTP, d) TPP, e) TPP-Pi-[Ti]Mag, f) Pi-[Ti]Mag, g) Pi-[Al]Mag and h) control, no photocatalyst.

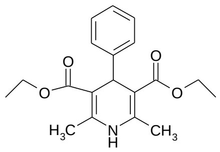
Figure 1B shows methidathion degradation kinetics using different catalysts. The control test (curve a), demonstrate the direct pesticide photodegradation exist, but are not well pronunciated, less than 9 % at 300 min. For the sample of TiO_2 pillared magadiite containing TPP was noticed a relatively low degradation degree, compared with others catalysts slower, at 180 min just 60 % and than seems desativate itself. A similar behaviour was observed for TPP in homogeneous condition, although more efficient and continued, leading to avery good degradation, 91 % at 300 min. Theother three catalysts have a very similar efficiency, for TPTP a bit inferior. For these three materials was noticed a strong initial degradation, from 67 up to 79 % with just 10 min, culminating to an almost complete degradation, 95 up to 99 % at 300 min. Photophysical experiments proved the involvement of an electron-transfer mechanism for dyes containing samples, most probaly from a ground state complex formed between substrate and catalyst.

Substituent and media effect on the photochemical behaviour of 4-aryl-1,4-dihydropyridines

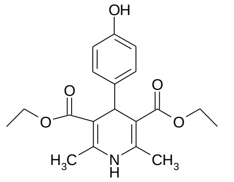
Nancy Pizarro[1], Karina Cabezas[1], Javier Morales[2], Germán Günther[3]
[1]Universidad Andrés Bello, Depto. de Ciencias Químicas, República 275, Santiago, Chile. [2]Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Depto. de Ciencias y Tecnología Farmacéutica, Santiago, Chile. [3]Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Depto. de Química Orgánica y Fisicoquímica, Laboratorio de Cinética y Fotoquímica, Santiago, Chile.

A great number of therapeutic drugs have been related to induce photoallergic or phototoxic effects. Among them, we are interested in 4-aryl-1,4-dihydropyridines, compounds belonging to a family of substrates widely used as antihypertensive drugs. The use of these calcium channel blockers in long term treatments has been associated with adverse photosensitive effects at skin level. In previous researches,[1,2] different photophysical and photochemical behavior have been reported for antihypertensive 4-aryl-1,4-dihydropyiridines depending on the substituent present on the phenyl ring. Also, it has been found that the capacity of these drugs to generate singlet oxygen depends on the medium polarity and on the 4-aryl moiety bearing different substituents. They are also classified as good scavengers of singlet oxygen, and there is a proposal for the reaction mechanism with reactive oxygen species.[3]

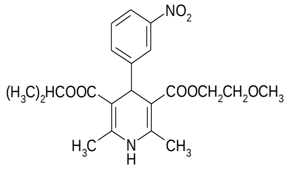
This work is focused on the kinetic comparison of photodegradation behaviour of 1,4-dihydropyridine bearing electron-donor (A, B) and electron-withdrawing (C, D) substituents on the 4-aryl moiety. We found that the presence of an electron-donor substituent on the 4-aryl moiety (or the absence of electron-withdrawing ones) diminishes the photodecomposition rates of 4-aryl-1,4-dihydropyridine. We also studied the photodecomposition of these compounds in solvents of different polarities. For comparison, the results of the photodegradation of these substrates in micelles were also included. As the nature of the head of surfactant (ionic or nonionic) could be important to modulate the photo-reactivity of these drugs, different kind of surfactants like sodium dodecyl sulfate micelles (SDS, anionic), dodecyl-pyridinium chloride micelles (DPC, cationic) or mono lauryl sucrose ester micelles (MLS, nonionic) were employed. The results have shown that the rate of the photodegradation is affected in different way by the media depending on the kind of substituent present on the 4-aryl moiety. In addition, compounds A and B were not able to generate singlet oxygen, but they are relatively good scavengers of this reactive species, because overall rate constant of singlet oxygen deactivation by these compounds are in the order of 10^5 to 10^6 $M^{-1}s^{-1}$.



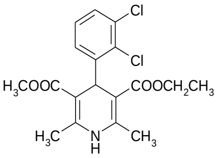
A



B



C



D

Acknowledgements: This work was supported by Project UNAB_DI_32_10R, Fondecyt grants 1080412 and 1110866.

References:

[1] P. Pavez, M. V. Encinas. Photochem. Photobiol. 2007, 83(3), 722-729.
[2] N. Pizarro, G. Günther and L. J. Nuñez-Vergara, J. Photochem. Photobiol. A, 2007, 189, 23-29.
[3] N. A. Pizarro-Urzua and L. J. Nuñez-Vergara, J. Photochem. Photobiol. A, 2005, 175, 129-137.

Photophysical and photobiological properties of phenylthio zinc-phthalocyanine photosensitizer into polymeric nanoemulsion applied to Photodynamic Therapy

Fernando L. Primo[1], **João M. Gonçalves**[1], **Juliana C. Junqueira**[2], **Antonio C. Tedesco**[1*]

[1]*Departamento de Química, Laboratório de Fotobiologia e Fotomedicina, Centro de Nanotecnologia e Engenharia Tecidual de Ribeirão Preto, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, 14040-901*

[2]*Universidade Estadual Paulista Júlio de Mesquita Filho, UNESP, Faculdade de Odontologia de São José dos Campos, Biociências e Diagnóstico Bucal*
São José dos Campos-SP, Brazil.

The main objective of the research project was to develop and characterize a nanostructured material to controlled release of photosensitizer phenylthio zinc-phthalocyanine (ZnPc-Phthio), to use in microbiological inactivation and neoplastic phototreatment based on photodynamic mechanisms [1]. ZnPc-Phthio was entrapped on polymeric nanoemulsion (NE) [2]. This nanodrug delivery system consist of the oily core with a water phase dispersant, which was prepared employing the interfacial spontaneous emulsification method described by Oliveira et al 2004 [3]. Physicochemical characterization was performed using the dynamic light scattering for determination of particle size, polydispersity index and zeta potential. The steady-state spectroscopic studies were performed by determining the absorption and fluorescence emission profile in the UV-visible to the ZnPc-Phthio/ethanol and ZnPc-Phthio/NE. The analysis of dynamic light scattering enabled the determination of physicochemical parameters of the formulation, which exhibited a particle size of 194.3 (± 5.7) nm, polydispersity index of 0.19 (± 0.04) nm and zeta potential of -52.8 (± 9.7) mV. Results show that the nano drug delivery system developed with nanotechnology has features with submicron particle size (d <300 nm), and a polydispersity index suitable for homogeneous systems monodisperse, with an absorption maximum at 685 nm and fluorescence emission centered at 694 nm (excitation at 615 nm). Cytotoxicity curve as evaluated from MTT protocol [4] to ZnPc-Phthio/NE incubated on human oral squamous cell carcinoma (OSCC) to determine non-toxicity dose range (< 5.0 µmol/L). These results are crucial for the development of future *in vitro* and *in vivo* protocols using phototherapy to treatment of oral oncologic diseases and microbiological photoinactivation. The controlled release of photosensitizers drugs is a promising and innovative therapeutic strategy that uses the nanotechnological advantages as an additional therapy available for dentistry.

[1] Seven et al., Journal of Porphyrins and Phthalocyanines, 12, 2008, 953-963.
[2] Primo et al.; Journal of Nanoscience and Nanotechnology, v. 8, p. 5873-5877, 2008
[3] Oliveira et al., Química Nova, 27(1), 2004, 131-138.
[4] Mosmann, T.; Journal of Immunological Methods, v. 65, p. 55-63, 1983.

Kinetic Study of the Reactions of Sulfate Radical Anions with Phenantrene in Aqueous Solutions

Fabricio Ragone[1], **Verónica C. Mora**[1,2], **Janina A. Rosso**[1]
1 Centro de Investigación y Desarrollo en Fermentaciones Industriales (CINDEFI), Facultad de Ciencias Exactas, UNLP, Argentina.
2 Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, UNLP, Argentina. janina@inifta.unlp.edu.ar

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental contaminants which derived from a variety of anthropogenic sources involving mainly incomplete combustion of organic matter and by industries. It has been reported that many PAH show a high toxic, carcinogenic, and mutagenic potential. They are hazardous to ecosystems and human health. Therefore, it is important to investigate the fate of PAH in aquatic environments and find a way to eliminate them or reduce their toxicity.

In-situ chemical oxidation (ISCO) involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical species. Persulfate (PS) is the newest form of oxidant currently being used for ISCO. PS can be chemically, photochemically, or thermally activated to generate the stronger oxidant sulfate radicals ($SO_4^{\cdot-}$), which are the main oxidant species. Thus, their reactivity with the contaminant studied is the first parameter to be considered.

In this work, we investigate the reactivity of $SO_4^{\cdot-}$ radicals with phenanthrene, as a model substance, the reaction mechanism and products formed.

Flash-photolysis experiments were carried out with conventional Xenon Co. model 720C equipment with modified optics and electronics. To avoid product accumulation, each solution was irradiated only once. Photolysis of PS ($\lambda < 300$ nm) was used as a clean source of $SO_4^{\cdot-}$ radicals. The rate of decay of SO4.- radical ($\lambda = 450$ nm) increase with [PHEN], as shown in **Figure 1**, for [PS] = 5×10^{-3} M without PHEN (upper trace) and with [PHEN] = 0.3 μM (lower trace).

The experimental traces could be well fitted to pseudo-first order decay, with apparent rate constant (b /s^{-1}). The slopes of the linear plots in ***inset*** **Figure 1** (b /s^{-1} vs, [PHEN]) yield the bimolecular rate constant ***k*** ($SO_4^{\cdot-}$ + FEN) = $(3.2 \pm 0.8) \times 10^9$ M^{-1} s^{-1}.

Experiments performed with higher concentration of PHEN (1.3 μM) indicated the formation of a transient species. **Figure 2** shows the spectrum at 1×10^{-3} s after the flash and the decay observed at 300 nm (***Inset*** **Figure 2**).

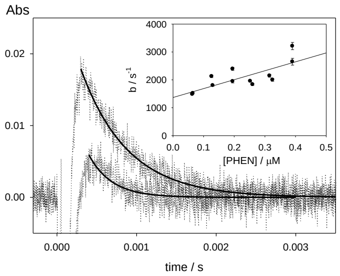


Figure 1: $SO_4^{\cdot-}$ decays obtained at 450 nm with [PS] = 5×10^{-3} M without PHEN (upper trace) and with [PHEN] = 0.3 μM (lower trace). Lines correspond to exponential fittings. ***Inset***: Plot of the pseudo-first-order rate constant b versus the molar concentration of PHEN.

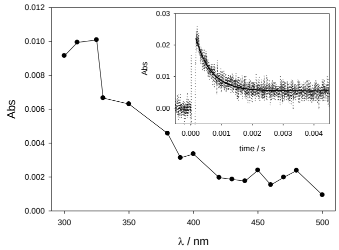
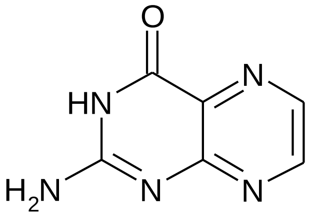


Figure 2: Absorption spectrum of the transients observed 1×10^{-3} s after the flash irradiation of [PS] = 5×10^{-3} M with [PHEN] = 1.3 μM. ***Inset***: Experimental absorbance profile obtained at 300 nm.

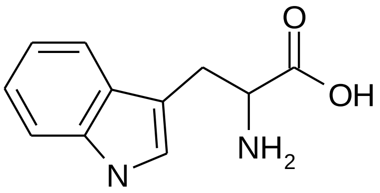
Tryptophan photosensitization by pterin

<u>Virginie Rahal</u>,[2] Mariana Paula Serrano,[1] Carolina Lorente,[1] Patricia Vicendo,[2]
Esther Oliveros,[2] Andrés H. Thomas,[1]
[1] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Fac. Cs. Exactas,*
UNLP, CCT La Plata-CONICET. CC 16, Suc. 4, (1900) La Plata, Argentina.
E-mail: athomas@inifta.unlp.edu.ar
[2] *Laboratoire des IMRCP, UMR CNRS/UPS 5623, Université Paul Sabatier (Toulouse III), 118,*
route de Narbonne, F-31062 Toulouse cédex 9, France. E-mail: vicendo@chimie.ups-tlse.fr

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 act as photosensitizer through type I (electron abstraction) and/or type II (the production of singlet molecular oxygen ($^1O_2$)) mechanisms. Moreover, pterin photoinduces DNA damage and oxidizes 2'-deoxyguanosine and 2'-deoxyadenine 5'-monophosphates (dGMP, dAMP)[2,3] *via* an electron transfer process. Due to the structural similarity with guanine and its low redox potential, tryptophan may be also a potential target for pterin mediated oxidation.



Pterin



Tryptophan

To evaluate the capability of pterin (Ptr) to photosensitize tryptophan, aqueous solutions containing both compounds were exposed to UV-A irradiation (320-400 nm) under different experimental conditions. The photochemical reactions were followed by UV/VIS spectrophotometry, HPLC, and an enzymatic method for H_2O_2 determination. In adition, fluorescence quenching experiments were performed.

During irradiation of solutions containing Ptr and Tryp, an increase of the absorbance at 340 nm was observed. HPLC analysis clearly showed that this photoreaction occurred only in the presence of oxygen and led to a high consumption of Tryp, whereas the amount of Ptr remained stable. These results suggest that Tryp may be oxydized by pterin *via* a mechanism involving, at least in part, an electron transfer process.

This reaction yields different photoproducts as shown by HPLC analysis. These preliminary results point out for the first time that pterins may not only photosensitize nucleic acids but also proteins *via* a complex reaction mechanism. Investigations are under progress to better characterize this original photoreaction.

[1] Lorente, C.; Thomas, A. H.; *Acc. Chem. Res*. **2006**, *39*, 395-402

[2] Petroselli, G.; Dántola, M. L.; Cabrerizo, F. M.; Capparelli, A. L.; Lorente, C.; Oliveros, E.; Thomas, A. H.; *J. Am. Chem. Soc.* **2008,** 130, 3001–3011.

[3] Petroselli, G.; Erra-Balsells, R.; Cabrerizo, F. M.; Lorente, C.; Capparelli, A. L.; Braun, A. M.; Oliveros, E.; Thomas, A. H.; *Org. Biomol.Chem.* **2007,** 5, 2792–2799

NORHARMANE, A NATURALLY OCCURRING PHOTOSENSITIZER: PHOTOOXIDATION OF 2´-DESOXYADENOSINE-5´-MONOPHOSPHATO

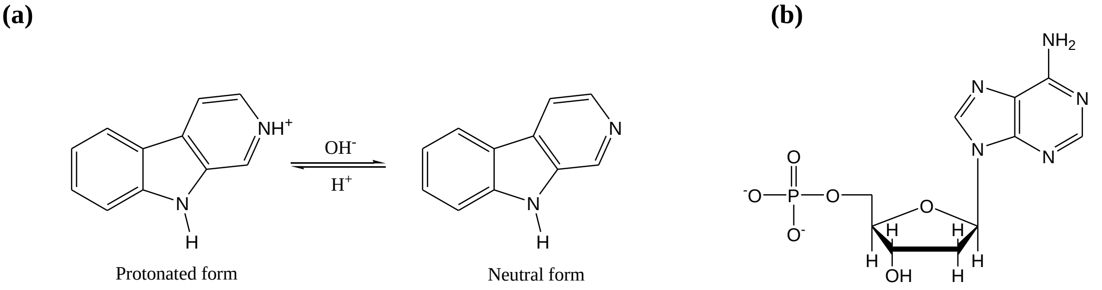
M. Micaela González[1], Federico A. O. Rasse-Suriani[1], Matías Alés-Gandolfo[2], Mariano Farace[2], Santiago Roldan[2], Rosa Erra-Balsells[1], Franco M. Cabrerizo[2]

[1] CIHIDECAR-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, 3p, Cdad. Universitaria (1428). Buenos Aires, Argentina.
[2] IIB-INTECH-UNSAM-CONICET. Camino circunv. Laguna Km 6. CC 164 (7130). Chascomús, Argentina.
E-mail: fcabrerizo@intech.gov.ar

UV-A radiation (320–400 nm) induces damages to the DNA molecule and its components through photosensitized reactions. Norharmane is an alkaloid widespread in biological systems showing photosensitizing properties. Upon UV-A radiation, norharmane is able to induce chromosome damage in mammalian cells,[1] and/or to photoinduce DNA relaxation.[2] Although these, the mechanisms involved in those processes are, to date, nevertheless still poorly understood.

In the present work, we have studied the capability of norharmane to induce 2´-desoxyadenosine-5´-monophosphate (dAMP) photooxidation, in aqueous solution, upon UV-A excitation. The effect of pH was evaluated and the participation of reactive oxygen species (ROS), such as hydroxyl radical ($HO^{\bullet}$), superoxide anion ($O_2^{\bullet -}$) and singlet oxygen ($^1O_2$) was investigated. A strong dependence of the dAMP photosensitization on the pH was observed. The extent of the reaction was shown to be higher in the experiments performed at pH 4.7 than those performed at pH 10.2. Kinetic studies using ROS scavengers revealed that the chemical reactions between ROS and dAMP are not the main pathways responsible for dAMP photooxidation. Further analysis suggest that the predominant mechanism takes place, most probably, via electron transfer reactions (*i.e.*, type I mechanism) from the single excited state (S_1) of the protonated form of norharmane.

In addition, the chemical nature of the photoproducts formed upon photosensitization was characterized by mass spectrometry (ESI-MS and UV-MALDI-TOF-MS).



Scheme 1. (a) Chemical structures of norharmane and the acid-base equilibrium observed in aqueous solution, in the pH range 3-11. **(b)** Chemical structure of 2´-desoxyadenosine-5´-monophosphate (dAMP).

---

[1] K. Shimoi, H. Kawabata, I. Tomita, *Mutat. Res.* **1992**, *268*, 287.

[2] M. M. Gonzalez, M. Pellon-Maison, M. A. Ales-Gandolfo, M. R. Gonzalez-Baró, R. Erra-Balsells, F. M. Cabrerizo, *Org. Biomol. Chem.*, **2010**, *8*, 2543

A Kinetic Study of the Crosslinking of Lysozyme by Photoinduced Generation of Side-Chain Tyrosyl Radicals

Luis A. Dorado, Valentina Rey, and Claudio D. Borsarelli
Instituto de Química del NOA (INQUINOA-CONICET). Universidad
Nacional de Santiago del Estero, Av. Belgrano (S) 1912. 4200-Sgo del
Estero, Argentina. E-mail: cborsarelli@yahoo.com.ar

Protein oxidation results in severe losses of biological functionality due to changes on the structure and/or conformation of the native protein. Depending on the type of oxidative agent and oxidation degree, the damage of the protein can result in peptide bond breakdown, aminoacid residue modification, crosslinking, etc. Lysozyme (LYZ) or muramidase, a 14.4 kD antimicrobial protein, is very abundant in a number of secretions, such as tears, saliva, human milk, mucus, and in egg white. LYZ has been used as preservative in foods. In the present work, we have studied the formation of *covalent* oligomeric species of LYZ by blue-light photosensitization of the metal coordination complex ruthenium (II) tris-bipyridine $Ru(bpy)_3^{2+}$ in the presence of ammonium persulfate (APS).

Several spectroscopic techniques (stationary and dynamic UV/Vis absorption and fluorescence) together with the analysis of SDS-PAGE were used to characterize the photocrosslinked products of LYZ. The formation of the covalent oligomeric species (dimer, trimer, …*n*-mer) was proportional with the irradiation time, figure 1.

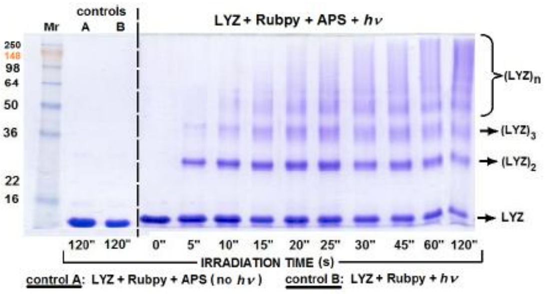


Fig. 1

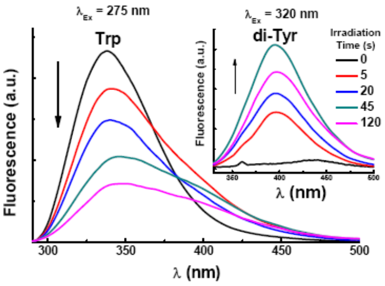


Fig. 2

The structural changes were parallel with UV absorption increases at 320 nm, quenching of the intrinsic protein fluorescence at 340 nm together with the increment of fluorescence at 405 nm, figure 2. All this features are indicative of the formation of di-tyrosine (di-Tyr). Laser-flash photolysis experiments demonstrated the formation of tyrosyl radical by electron-transfer reaction of the oxidized $Ru(bpy)_3^{3+}$ with Tyr. Finally, the antimicrobial activity of these species was compared with that of native LYZ.

Acknowledgments: authors gratefully acknowledges to CONICET for financial support. CDB also thanks FONCyT for supporting the PICT2006-01090 and the Alexander von Humboldt Foundation of Germany for a Georg Forster Fellowship

Detection of low quantum yield fluorophores and improved imaging times using metallic nanoparticles

M. Julia Roberti[1,3]***, L. Estrada**[2]**, Valeria Levi**[3]**, Oscar Martinez**[2]**, Pedro Aramendía**[1]
*1INQUIMAE-CONICET, 2Physics Department and 3Biological Chemistry Department, Faculty of Exact and Natural Sciences, University of Buenos Aires, Ciudad Universitaria (1428), Buenos Aires, Argentina.*juliaroberti@qi.fcen.uba.ar*

Fluorophore-metal nanoparticle systems constitute excellent biosensors for applications in the field of cellular biology[1]. Gold NPs (AuNPs) can enhance the emission of fluorophores through interaction of the NP plasmon with the molecule absorption and emission moment[2]. In previous works[3,4], we modeled this effect on AuNPs coupled to model fluorophores. We showed an enhancement in brightness and photostability for the fluorophores interacting with AuNPs, while the extent of this enhancement was spatially reduced up to 10 nm.

Here, we address this enhancement effect in vitro and in cells using fluorescence microscopies. The enhancement in brightness in imaging experiments in vitro was assessed by using Au-SiO2 core-shell nanoparticles deposited on glass, and a ~13-fold enhanced contrast for weakly fluorescent molecules in the vicinity of the nanoparticles was observed. A significant increase in the fluorophore photostability rendering longer imaging times was obtained for fluorophores interacting with Au nanoparticles incorporated by endocytosis in cells. We employed AuNPs combined with different fluorophores, and easily internalized through endocytosis. We confirmed the enhancement of fluorescence on endocyted AuNPs interacting with fluorescently-labeled actin filaments, evidenced as an improved contrast and prolonged imaging times for those fluorophores associated to the filaments and at close vicinity to the nanoparticles[4].

This work shows the possibility of detecting intrinsic fluorescence of biomolecules and obtaining longer imaging times at the single molecule level, with subdiffraction resolution. The combination of AuNPs and fluorophores may be advantageously applied in multiple trafficking studies by stationary and time-solved microscopies, coupled to high resolution EM microscopy to characterize the localization and morphology of the targets.

1. Shaoqin Liu and Zhiyong Tang. J. Mater. Chem. 20, 24–35 (2010).
2. Ghosh, S. K. and T. Pal.. Phys. Chem. Chem. Phys. 11, 3831-3844 (2009).
3. Estrada, L. C., P. F. Aramendía, and O. E. Martínez. Opt. Express 16, 20597-20602 (2008).
4. L. Estrada, M. Julia Roberti, V. Levi, P. F. Aramendía, and O. Martínez. Manuscript in preparation.

Photophysics of Eosin Y Absorbed on Microcrystalline Cellulose

Hernan B. Rodriguez,(1) **Paulo Duarte,**(2) **Isabel Ferreira Machado,**(2) **Luis Filipe Vieira Ferreira,**(2) **and Enrique San Román**(1)

(1) *INQUIMAE / DQIAyQF, Facultad de Ciencias Exactas y Naturales, UBA, Ciudad Universitaria, Pab II, C1428EHA, Buenos Aires,Argentina, hbr@qi.fcen.uba.ar*

(2) *Centro de Química-Física Molecular, Complexo Interdisciplinar, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

The photophysical behavior of Eosin Y absorbed on microcrystalline cellulose particles was studied by steady state and time resolved diffuse reflectance and emission spectroscopies. Emission measurements include phosphorescence and direct and delayed fluorescence. Solid samples, spanning two orders of magnitude in dye concentration, were prepared by evaporation of the solvent from suspensions of weighed amounts of cellulose in ethanol containing known concentrations of the dye. Measurements were performed in previously dried thin and optically thick layers.

Diffuse reflectance spectra show some deviations pointing to the occurrence of ground state interactions at the highest concentrations. Thick layer fluorescence spectra show the typical effects of emission reabsorption by the dye. Interactions between excited and ground state molecules are also observed as a fluorescence red shift on increasing the dye concentration in thin layers. Fluorescence quantum yield measurements, presently underway, show after correction by reabsorption a significant decrease at the highest concentrations, attributed to long range energy transfer and trapping. The same reason causes shortening of fluorescence lifetimes as concentration increases.

.

Phosphorescence and delayed fluorescence were measured at room temperature. No degassing was needed as the cellulose environment protects the triplet state from oxygen quenching. A complex decay independent of sample concentration was found. Phosphorescence spectra show a pronounced blue shift with time. A unique spectrum is obtained for all samples at all times after shifting spectra to achieve a common maximum.

Delayed fluorescence spectra are sample-dependent because of light reabsorption. Decays are also complex: bimodal lifetime distributions similar to those found for phosphorescence decays, except for the weight factors of the long and short time contributions are obtained. Spectra are somewhat affected by emission from the supporting material and the phosphorescence blue tail. Results are consistent with thermally activated delayed fluorescence. However, low temperature experiments will be performed in the near future to ascertain the possible participation of triplet-triplet annihilation.

Results are interpreted in terms of site heterogeneity: long lived, more energetic triplet states coexist with short lived, less energetic ones. Lifetime distribution analysis is consistent with the long lived states corresponding to dye molecules tightly entrapped within cellulose chains. Short lived states result from dye molecules in more flexible environments. Experimental results and qualitative and quantitative arguments leading to the present conclusions will be presented.

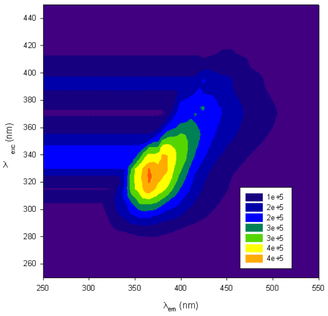
Photochemical Synthesis of Silicon Nanoparticles

<u>Juan José Romero</u>[1]**, María Laura Dell' Arciprete**[1, 2]**, Mónica C. González**[1, 2]**.**
[1]*Facultad de Ciencias Exactas, UNLP, calle 115 y 47, La Plata, Argentina,* [2]*INIFTA, Dpto. de Química, FCE, UNLP. CC 16 Suc. 4, (1900) La Plata, Argentina.*

Silicon nanoparticles (Si-NP) of 1 to 5 nm size show photoluminescence because of the quantum confinement effect. In consequence, the emission and excitation spectra and other photophysical properties will depend on the NP size and the chemical nature of its surface. The strong luminescence of Si-NP, their capacity for singlet oxygen ($^1O_2$) generation, and the richness of silicon surface chemistry suggest that Si NP would be useful in various biological applications as optical sensors and agents for cancer therapy[1,2]. Therefore, the search for facile, efficient, and low-cost synthetic routes is an important goal for silicon nanoparticles applications. In particular, the obtainment of Si-NP with the minor impurities is a fundamental requirement for future applications. The present work describes a first photochemical approach to satisfy this need.

Solutions of different concentrations of $SiCl_4$ in cyclohexane were prepared and irradiated in the absence of O_2 with light of 350 ± 20 nm at different intensities. Depending on [$SiCl_4$], light intensity and irradiation time, the solutions develop photoluminescence with emission-excitation spectra coincident with those of 1 nm size Si-NP obtained with wet chemical methods (see the figure below). The experimental conditions were optimized to maximize the photoluminescence in order to obtain a sufficient amount of product for its chemical characterization by FTIR, UV-Vis spectroscopy, and XPS.

The image shows the emission-excitation matrix of the product obtained by irradiation of a $SiCl_4$ 2.6 M solution during 180 minutes, in Ar atmosphere. After the synthesis, the solution was mixed with O_2 for an hour, and then the matrix was taken.



Considering that $SiCl_4$ does not absorb in the 330 – 370 nm irradiation wavelength, it is suspected that either trichlorosilane or $SiCl_3OH$, common impurities present in commercial accessible $SiCl_4$ batches and in aged reactants[3,4], respectively, initiate a chain reaction leading to the formation of Si-NP.

Following investigations involve the control of particle size and surface derivatization through the variation of easily adjustable parameters, such as initiators, reactant concentration, reaction time, radiation intensity, etc.

---

[1] Swihart, M. T. Nanotechnology in Biology and Medicine, Methods, Devices, and Applications; CRC Press: Boca Raton, USA, 2007; Vol. 4.

[2] Llansola Portolés MJ, et al. Silicon Nanoparticle Photophysics and Singlet Oxygen Generation. Langmuir 2010, 26: 10953-10960.

[3] Gooden, R. Photooxidation of Trichlorosilane in Silicon Tetrachloride, Inorg. Chem. 1983, *22***,** 2212-2215.

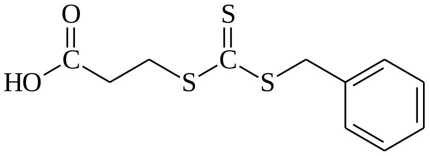
[4] Krylov, V. A., Salganskii, Yu. M., Chernova, O. Yu. Highly Sensitive Determination of Carbon- and Hydrogen-Containing Impurities in Silicon Tetrachloride by Gas Chromatography. J. Analytical Chem. Chemistry and Materials Sci., 2001, 56, 844 -849.

Photoinduced polymerization of N,N'-dimethylacrylamide by reversible addition-fragmentation chain transfer polymerization.

M. Victoria Encinas, Ana M. Rufs, Andrea Valdebenito
Facultad de Química y Biología, Universidad de Santiago de Chile, Chile.

The synthesis of well-defined polymer architectures with low polydispersity has acquired special importance in the last years. Among the most used techniques to obtain these materials is the reversible addition fragmentation chain transfer polymerization (RAFT). Frequently the radicals that initiate the free radical polymerization are produced by the thermal photocleavage of azo-compounds. Therefore, they are carried out at high temperatures. Radicals also have been obtained at room temperature using γ-radiation. However, it is important to consider the disadvantages associated to these types of energy sources, in particular, in polymerizations that involve biological compounds. Only few studies have been reported at room temperature in mild conditions. Dithiocarbamates or trithiocarbonates are used as chain transfer agents (CTA).

In this work, we report the polymerization of N,N'-dimethylacrylamide (DMA) at 25 ^{o}C using as photoinitiatiator the radicals produced from the photodecomposition of the CTA of the RAFT polymerization, 3-(benzylsulfanylthiocarbonylsulfanyl) propionic acid (BSP) (Structure 1), employing 360 nm irradiation. The goal of this work is the use of the BSP as photoinitiator as well as CTA.



Structure 1

BPS was prepared as previously described (Stenzel and Davis, J Polym Sci A 40, 2002, 4498). The polymerization was carried at 20 ^{o}C, under N_2, and irradiation of 360 nm. The monomer conversion was followed by ^{1}H MNR spectroscopy. The controlled polymerization was confirmed by the lineal dependence of the polymer molecular weight with the conversion, and the low polymer polydispersity (<1.2).

The photocleavage of BPS was studied following the formed products after the irradiation at 300 or 360 nm. The 2D MNR spectroscopic analysis of products showed that the photocleavage is produced at the S-C bond corresponding to the propionic acid. This allowed obtain a polymer with a tritiocarbonyl group bound to the end of the polymer chain. Also, we used this polymer as macrophotoiniator for the polymerization of a second monomer. In this way we could obtain an amphiphilic block copolymer.

Acknowledgements: Fondecyt (grant # 1070123) for financial support.

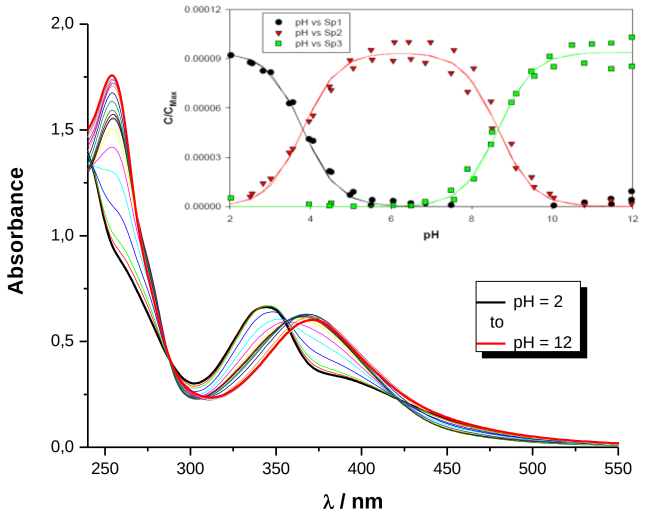
Absorption and emission spectroscopy of a new water-soluble tricarbonyl Re(I) complex. Solvent and pH dependence.

Fabricio Ragone, Sebastián García-Einschlagh and Gustavo T. Ruiz
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA, UNLP, CCT La Plata-CONICET), Diag. 113 y 64, Sucursal 4, C.C. 16, 1900 La Plata, Argentina
e-mail: gruiz@inifta.unlp.edu.ar

A new $Re^{I}(CO)_3L_1L_2$ complex has been obtained and characterized by Rx, ^{1}H-RMN, IR, UV-MALDI and ESI. The ligand L_1 = 2-amine-4-pteridinone, pterin, is a heterocyclic compound of biological interest and $L_2 = H_2O$.

Here we show preliminary results about spectroscopy´s studies of solutions of the complex in different solvents and pH´s. UV-Vis absorption spectra show intense bands in the UV range, $\lambda_{máx}$ ~ 345 nm. These spectral features are almost identical with those found in the electronic spectrum of the free pterin ligand and are therefore assigned to π–π* excitations in the aromatic ligand fragment. The solutions of complex are coloured and their absorption in the visible part of the spectrum exhibit typically intense and solvatochromic long-wavelength metal-to-ligand charge transfer (MLCT) transitions from the metal dπ to the lowest lying ligand π* orbital. These bands experience an hypsochromic shift with increasing solvent polarity, feature that confirms this assignment. The strong dependence on pH suggests the existence of two acid-base equilibrium. Emission spectra in aqueous solutions of the complex show the luminescence which was attributed to a desactivation from the lower π–π* ligand-localized state, as suggested from the emission spectrum of the free pterin. However, the emission from IL and MLCT excited states have been observed in organic solvent. Moreover, the observed luminescence shows a strong dependence on oxygen concentration. The calculated values for both emission quantum yield and lifetime in all solvents tested will be compared with those reported to free pterins.

These photophysics properties lead us to believe in this kind of complex to be used in the development of new photochemical sensors.



OLIGO(BENZO[C]THIOPHENE-2-OXIDE) A POLY(ISOTHIANAPHTHENE) DERIVATIVE WITH GOOD PHOTOVOLTAIC PROPERTIES

Christian Sánchez[1], **Jean-Christian Bernede**[2], **L. Cattin**[2]
[1)] Instituto de Química, Facultad de Ciencias, Universidad Austral de Chile, Avda. Las Encinas 220, Campus Isla Teja, Valdivia, Chile.[2)] UNAM, Moltech Anjou, UMR 6200, 2 rue de la Houssinière, BP 92208, Nantes, F-44000 Francia

Photovoltaic cells made of conjugated polymeric materials have a great technological potential as an alternative source to generate electrical power [1,2]. One of the limiting parameters of these photovoltaic polymers is the mismatch between their absorption spectrum and that of the terrestrial solar spectrum. The use of low-band gap polymers (Eg lower than 2.0 eV) is a viable method to expand the absorption spectrum of solar cells and therefore to increase their efficiency [3,4]. To improve the performances of organic solar cells, many efforts are focused on the synthesis of new compounds whose absorption spectra allow a better matching with that of the solar spectrum. To that end, a new poly(isothianaphthene) derivative, with low band gap, called, poly(benzo[c]thiophene-2-oxide), (Fig. 1) was synthesized and characterized by elemental analysis, UV-vis, FT-IR, ^{1}H-NMR and XPS spectroscopy. Oligomers were obtained from 1,3-dihydrobenzo[c]thiophene-2-oxide by oxidative coupling using sulphuric acid in methanol as oxidizing agent in the presence of air. The oligomer has a band gap of 1.75 eV measured by Visible absorption edge. Its LUMO was measured by cyclic voltammetry (LUMO = -3.77 eV). From the LUMO and band gap values, the HOMO was estimated to be -5.52 eV. Oligomeric film prepared under high vacuum was probed in photovoltaic device as electron donor. Photovoltaic device based on Glass/ITO/ MoO_3(3nm)/poly(benzo[c]thiophene-2-oxide) (15 nm)/ fullerene-C_{60}(40 nm)/ Bathocuproine (BCP) (9 nm)/Aluminium have been probed (Fig. 2). The active area of the cells was 0.16 cm^2. These cells showed a power conversion efficiency of 1.24% under the illumination of AM1.5 at 100 mW/cm^2 (Fig. 3), which shows that this family of poly(isothianapthene) oligomers have promising properties for photovoltaic applications.

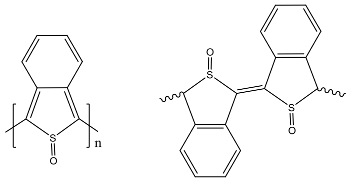


Fig. 1: Oligomeric structures

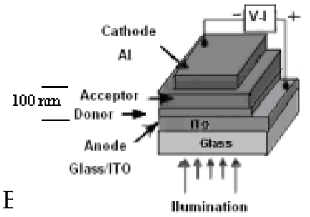


Fig. 2: E
/ of 1.24%

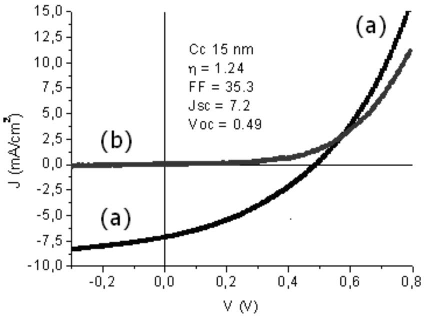


Fig. 3: I vs V curves a) absence of light and b) presence of light

References

[1] D. Wohrle, D. Meissmer, Organic Solar Cells, Adv. Mater. 3 (1991)129

[2] H. Spanggaard, F. C. Krebs, A brief history of the development of organic and polymeric photovoltaics, Solar Energy Material Solar Cells, 83 (2-3) (2004) 125

[3] S.E. Shaheen, D. Vangeneugden, R. Kiebooms, D. Vanderzande, T. Fromherz, F. Padinger, C.J. Brabec, N.S. Sariciftci, Low band-gap polymeric photovoltaic devices, Synth. Met. 121 (2001) 1583

[4] K. Colladet, M. Nicolasa, L. Goris, L. Lutsen, D. Vanderzande, Low-band gap polymers for photovoltaic applications, Thin Solid Films, 451/452, 7 (2004).

Emission properties of dihydropterins in aqueous solutions

Mariana P. Serrano, Mariana Vignoni, M. Laura Dántola, Carolina Lorente and Andrés H. Thomas
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),
Departamento de Química, Fac. de Cs. Exactas, Universidad Nacional de La Plata, CCT La Plata-CONICET. CC 16, Sucursal 4, (1900) La Plata, Argentina. e-mail:
mariserr@inifta.unlp.edu.ar

Pterins, heterocyclic compounds derived from 2-aminopteridin-4-(3*H*)-one or pterin [1], are present in biological systems in multiple forms. They can exist in different oxidation states: oxidized (or aromatic) pterins and reduced pterins. Within the latter group, 7,8-dihydropterins and 5,6,7,8-tetrahydropterins are the most important derivatives due to their biological activity, *e.g.*, dihydroneopterin (H_2Nep) is secreted during the oxidative burst of stimulated macrophages [2], dihydrobiopterin (H_2Bip) and tetrahydrobiopterin are involved in the metabolism of aminoacids [3]. In addition, H_2Bip, biopterin (Bip) and other pterin derivatives accumulate in the skin of patients affected by vitiligo, a depigmentation disorder, where the protection against UV radiation fails due to the lack of melanin [4-5].

Upon UV-A excitation, unconjugated oxidized pterins present emission bands with maximum around 450 nm, relatively high fluorescence quantum yields ($\Phi_F > 0.10$) and fluorescence lifetimes (τ_F) in the range 2-14 ns. Dihydropterins are more complicated to work with because they are unstable in air-equilibrated solutions, undergoing oxidation with a rate depending on the chemical nature of the substituent [6]. In addition the emission of dihydropterins is very weak and, and the solutions prepared from chemicals of the highest purity commercially available are contaminated with small concentrations of oxidized pterins. For that reason, given that the absorption spectra of dihydropterins and oxidized pterins are in general more or less superimposed, the emission of the latter is a main interference in the analysis of the fluorescence of the former.

The aim of this work was to investigate the emission properties of dihydropterins in their neutral forms, in aqueous solutions upon UV-A irradiation. We have chosen for this study 6 pterin derivatives: 6-formyldihydropterin (H_2Fop), sepiapterin (Sep), dihydrobiopterin (H_2Bip), dihydroneopterin (H_2Nep), 6-hydroxymethyldihydropterin (H_2Hmp) and 6-methyldihydropterin (H_2Mep). In particular, we have investigated the emission spectra, determined the Φ_F and τ_F values, and discussed about the effects of the substituents on the emission properties.

References:

[1] D. J. Brown, *The Chemistry of Heterocyclic Compounds*, John Wiley & Sons, New York, 1988, **24**, 1-42.

[2] C. Huber, D. Fuchs and A. Hausen, *Journal of Immunology*, 1983, **130**, 1047-1050.

[3] C. A. Nichol, G. K. Smith and D. S. Duch, *Annu. Rev. Biochem.*, 1985, **54**, 729-764.

[4] K. U. Schallreuter, J. M. Wood, M. R. Pittelkow, M. Gütlich, K. R. Lemke, W. Rödl, N. N. Swanson, K. Hitzemann and I. Ziegler, *Science*, 1994, **263**, 1444-1446.

[5] H. Rokos, W. D. Beazley and K. U. Schallreuter, *Biochem. Biophys. Res. Commun.*, 2002, **292**, 805-811.

[6] M. L. Dántola, M. Vignoni, A. L. Capparelli, C. Lorente and A. H. Thomas, *Helv. Chim. Acta*, 2008, **91**, 411-425.

Photochemically Synthesized Cobalt Oxide Water Oxidation Catalyst

Benjamin D. Sherman,[1] Tse-Luen (Erika) Wee,[2] Juan C. Scaiano,[2] Devens Gust,[1] Ana L. Moore,[1] Thomas A. Moore[1]

Center for Bio-Inspired Solar Fuel Production and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604, USA.1 Centre for Catalysis Research and Innovation and Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada.2

A major obstacle in the pursuit of a viable artificial photosynthetic device for solar energy conversion to a fuel lies in the discovery of a cost and energy efficient water oxidation catalyst. Many of the efficient and stable water oxidation catalyst used to date have relied on expensive and scarce elements such as platinum, iridium, and ruthenium. The desire for society wide implementation of solar to fuel systems necessitates the development of new catalytic materials based on more earth abundant elements such as iron, manganese, or cobalt. Herein we present a photochemical procedure for the formation of Co_2O_3 which has demonstrated the catalytic oxidation of water to O_2 in solutions containing phosphate buffer. Our approach utilizes photo-induced radicals for the formation of Co_2O_3 particles from acetonitrile solutions containing Co_2+ ions. This procedure has allowed for both the production of particles containing only cobalt oxide as well as the deposition of the oxide on various surfaces including nanodiamonds, carbon felt, and mesoporous (semi)conducting layers. Electrochemical studies of the Co_2O_3 have shown the generation of high anodic currents at sufficiently positive potentials which have correlated to the generation of oxygen in solution as measured by a Clark electrode. The ability for controlling the deposition of the oxide could have important advantages in utilizing this material as a catalyst in photoelectrochemical systems. We are currently pursing its use in a porphyrin-based photoanode designed to carry out the light driven oxidation of water to oxygen.

A Porphyrin Stabilized Iridium Oxide Water Oxidation Catalyst

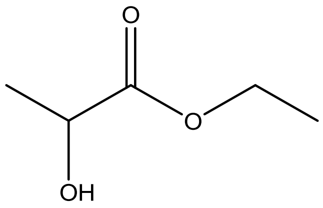
Benjamin D. Sherman,[1] Smitha Pillai,[1] Gerdenis Kodis,[1] Jesse Bergkamp,[1] Thomas E. Mallouk,[2] Devens Gust,[1] Thomas A. Moore,[1] Ana L. Moore.[1]
Center for Bio-Inspired Solar Fuel Production and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604, USA.[1]
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA.[2]

Integrating light absorbing materials to catalysts to drive the oxidation of an electron source and the reduction of a precursor to a fuel presents one of the principal challenges in producing photoelectrochemical devices for solar energy conversion. In pursuit of systems which can parallel the process of photosynthesis, we have investigated using porphyrin dyes as stabilizers for the formation of iridium oxide hydrate ($IrO_2 \cdot nH_2O$) colloidal solutions. Solutions of $IrO_2 \cdot nH_2O$ have been formed using a porphyrin bearing malonate-like functional groups at each of the four *meso* positions of the porphyrin ring. Cyclic voltammetry and monitoring of solution oxygen concentrations under constant applied potential have demonstrated the electrochemical catalytic activity of the porphyrin–$IrO_2 \cdot nH_2O$ complex for the oxidation of water to oxygen. Quenching of the porphyrin fluorescence in the complex implies strong interaction between the porphyrin and the $IrO_2 \cdot nH_2O$. We are now pursuing the use of other porphyrin molecules containing functional groups to allow for both the formation of the colloidal $IrO_2 \cdot nH_2O$ and then the subsequent immobilization of this complex on transparent semiconducting electrodes. This work marks progress toward developing a porphyrin-based photoanode for use in a photoelectrochemical water splitting cell capable of producing hydrogen fuel from water and sunlight.

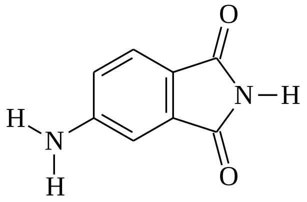
Ethyl Lactate: a Peculiar Solvent. The Photophysical Behavior of 4-aminophthalimide in Ethyl lactate-Water and Ethyl lactate-*n*-Heptane Mixture

Andrés M. Durantini[1], R. Darío Falcone[1], Elsa Abuin[2], Eduardo Lissi[2], Juana J. Silber[1] and N. Mariano Correa[1]
[1] Departamento de Química. Universidad Nacional de Río Cuarto. Río Cuarto. Argentina. Email jsilber@exa.unrc.edu.ar. [2] Universidad de Santiago de Chile, Facultad de Química y Biología, Santiago, Chile.

Ethyl lactate, EL, is a very adequate alternative green solvent that it shows many environmental, toxicological, technological and, economical advantages for many applications since it is non-toxic. It is known that large deviations from ideality are obtained when EL and water are mixed, which are related to the development of strong intermolecular hydrogen bonding between both molecules upon mixing. Despite some works that have attempted to investigate this interesting mixture, there are many facts that are still not well understood. On the other hand, interesting is the fact that EL is also completely soluble in *n*-heptane which makes EL a unique and interesting solvent to investigate. Our group aim to use this solvent to create new “green” organized systems however, it is crutial to understand the behavior of EL in homogeneous media.



LE



4-AP

The goal of our work is to gain insights on the different interactions that EL undergoes with water and n-heptane that makes EL soluble in both very dissimilar solvents. Thus, we have investigated the properties of EL-water and EL-*n*-heptane mixtures using absorption, steady state and time resolved emission techniques employing 4-aminophthalimide (4-AP) as a molecular probe. This dye exhibits the singular emission feature of compounds with an electron-donating moiety (the amino group) and an electron acceptor moiety (the carbonyl of the imido group) placed in the *para* position in a benzene ring and it is very sensitive to the hydrogen bond donor ability of its surrounding. The results show that both 4-AP absorption and emission bands shift bathochromically with the polarity and the hydrogen bond donor ability of the medium being much more sensitive to the hydrogen bond interaction upon excitation. In the EL-*n*-heptane mixture no effect of the *n*-heptane concentration is observed in the spectroscopic behaviour of 4-AP being the dye always solvated by EL through hydrogen bond interactions. On the other hand, a surprising situation is observed for 4-AP in water-EL mixture. The time resolved emission spectra (TRES) reveals an unexpected blue shifting with time upon water addition. It seems that the strong water-4-AP interactions produce multiple species in the 4-AP excited state that emits at different wavelengths. It seems that water stabilizes the blue-emitting species while the opposite stands for EL.

Interactions between the components of the Laponite/StyS system before photopolymerization.

Douglas Silva Machado, **Tatiana Batista, Carla Cristina Schmitt Cavalheiro and Miguel Guillermo Neumann**
Instituto de Química de São Carlos, Universidade de São Paulo, Brazil.

Recently much attention has been devoted to the development of clay/polymer composites due to some unique properties. On the other hand little is known about the properties of these systems prior to the photopolymerization process that may lead to the formation of nanocomposites. Previously, we have successfully synthesised photochemicaly Poly(styrenesulfonate) (pStyS) in presence of Laponite using Safranine O (SfH^+) as initiator. In this work we focus on the colloidal and photochemical characteristics of the interactions of the components (sodium styrenesulfonate (StyS), Laponite and SfH^+) before polymerization. Thus, Uv-vis absorption, fluorescence and flash photolysis of the reactional medium were studied. Small angle X-ray scattering (SAXS) was also used to determine parameters like the radius of gyration (Rg) and the second virial coefficient (A_2) to probe the interactions between Laponite, the monomer, and the initiator. In absence of clay, the absorption and fluorescence of the dye depend on the monomer concentration, but no changes were observed when Laponite was added. Flash photolysis experiments show that triplet lifetime, τ, of SfH^+ is also a function of the StyS concentration. In pure water, τ (SfH^+) was 65 µs, decreasing to 24 µs after adding 0.7 M of StyS. However, in presence of Laponite at same StyS concentration τ is the same than in water (65 µs). Isothermal adsorption analyses indicates after ~1 h, 98 % of SfH^+ was adsorbed on the clay surface, justifying the observed spectroscopy characteristics.

Suspensions of Laponite at different concentration were analysed by SAXS, in water, StyS, StyS/SfH^+ and NaCl. Table 1 summarizes the Rg (calculated by Guinier plots) and A_2 (calculated according to eq. 1) obtained from the SAXS curves of Laponite. Positive A_2 values indicate attractive interactions between the clay particles and solvent, more pronounced in NaCl, that binds to the surface charges. In StyS a destabilisation of the solution occurred, evidenced by the approximation to zero value. Both Laponite and StyS have negative charges, justifying the repulsion observed. Stabilization occurs when Safranine was added to the solution, indicating that even at low concentrations, the positive charge of the dye is sufficient to bind to the negative charge of Laponite and intermediate the interaction between the negatively charged StyS and Laponite. It is important to mention that previous studies indicate that the monomer interacts strongly with the clay surface, which is the place where the polymerization occurs. A schematic representation of the overall process is shown in Figure 1.

Table 1- Rg and A_2 for Laponite in different environments.

Environments	**Rg (nm)**	**A_2 (cm^3 g^{-1} mol) App.**
Water	12.2	8.61×10^{-4}
NaCl (0.5 M)	14.3	3.71×10^{-4}
StyS (0.5 M)	16.5	1.23×10^{-7}
StyS (0.5 M)/SfH^+(1×10^{-5}M)	16.7	1.19×10^{-4}

$$\frac{C}{I_0}=\frac{1}{kM}+\frac{2A_2C}{k} \qquad \text{eq. 1}$$

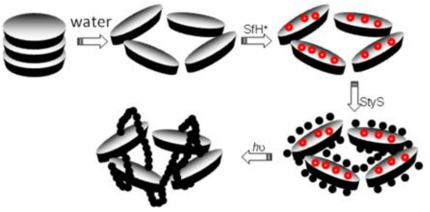


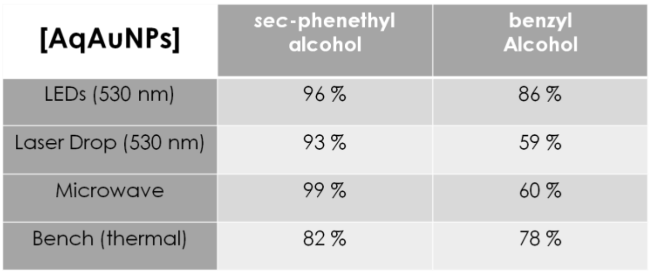
Figure 1: Schematic representation of the synthesis of pStyS/Laponite composites. Red circle represents SfH^+ and black circles StyS.

Acknowledgements: CNPq, CAPES, FAPESP and LNLS.

Plasmon Mediated Catalytic Oxidation of sec-Phenethyl and Benzyl Alcohols

Jazmín Silvero, Geniece L. Hallett-Tapley, María González-Béjar, José Carlos Netto-Ferreira, and Juan C. Scaiano*
Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa K1N 6N5, Canada

In organic and industrial chemistry, alcohol oxidations are one of the most widely exploited reactions due to the extensive use of ketones in the manufacturing of various products, such as paints and plastics. Conventional methods of oxidizing benzylic alcohols involve the use of chromates or permanganates, typically viewed as environmentally unfriendly oxidants; therefore current interests focus on the development of greener catalysts that efficiently oxidize these chemicals as effectively as the more traditional methods, while still offering high selectivity and the advantage of catalyst reusability and less toxic waste. Metallic nanoparticles (NP) seem to have a lot to offer in this field. In particular, AuNPs have shown interesting properties. In the present, work we use AuNP in aqueous solutions, obtained from reduction of Au^{3+} by photochemically-generated ketyl radicals.[1] The absorption of energy at 530 nm, the surface plasmon band (SPB) for spherical AuNP, results in a collective oscillation of the surface electrons of the AuNP. Moreover, the intermediate polarization of the NP surface electron *via* plasmon excitation can create rapid, localized heating of the NP surface allowing for harvesting of thermal energy. The dramatic increase in temperature within close proximity to the NP allows chemical reactions typically requiring high temperatures to be carried out in the microenvironment surrounding the AuNP at ambient, bulk temperatures. This effect is known as plasmon mediated catalysis (PMC).[2] In the present contribution, PMC is employed to successfully oxidize *sec*-phenethyl and benzyl alcohols in the presence of aqueous AuNP and H_2O_2 using laser drop techniques or light emitting diodes; the results are compared with microwave excitation. In all cases, good conversion to the corresponding ketone or aldehyde was observed (Table 1). A mechanism involving both photothermal and photochemical effects will be discussed.



[AqAuNPs]	sec-phenethyl alcohol	benzyl Alcohol
LEDs (530 nm)	96 %	86 %
Laser Drop (530 nm)	93 %	59 %
Microwave	99 %	60 %
Bench (thermal)	82 %	78 %

Table 1. Results of PMC of alcohol oxidation (% of ketone or aldehyde)

---

[1] Martin, M. *et al. J. Am. Chem. Soc.* **2008**, *130*, 16572
[2] Burda, C. *et al. Chem. Rev.* **2005**, *105*, 1025

Proton Transfer from 2-Naphthol to Amines in Supercritical Fluids

Sabrina Simoncelli[1], **Pablo A. Hoijemberg**[1], **M. Laura Japas**[2], **Pedro F. Aramendía**[1]
[1] INQUIMAE and Dto. Química Inorgánica. FCEN. Universidad de Buenos Aires. [2]
Gerencia Química CNEA. and Universidad Nacional de San Martín. Argentina.
simoncelli@qi.fcen.uba.ar

We report in this work the successful quantification of the dynamics of proton transfer from excited-state 2-naphthol to various amines in supercritical CO_2 ($scCO_2$) at 35 ºC and in the pressure range between 100 and 200 bar. 2-Naphthol is a photoacid that changes its pK_a in water from 9.5 in the ground state to 2.5 in the singlet excited state. Furthermore, the absorption but notably the emission spectra of the acid form and its conjugated base are easily distinguished. As proton acceptor, N-ethyldiisopropylamine (DIEA), triethylamine (TEA) and morpholine (MP) were used.

Absorption, steady state fluorescence emission and excitation spectra were measured as a function of amine concentration and pressure at 35ºC. Equilibrium constants for the proton transfer reaction in the ground state in cyclohexane and in $scCO_2$ indicate that this reaction is less effective in supercritical fluids (SCF) than in water or, even, cyclohexane. On the other hand, the difference in pK values for the proton transfer reaction in the ground and in the excited states is nearly 8 units, indicating that the change in acidity upon excitation in $scCO_2$ is as large as in water.

Our results show that, depending on the amine used, solvent effects on the absorption spectrum of 2-naphthol, or on the emission spectrum of 2-naphtholate, static or dynamic quenching of the excited state of 2-naphthol are observed. For DIEA and TEA, proton transfer yields anion emission, see Figure 1. Linear Stern-Volmer relations for the system 2-naphthol/DIEA were observed in $scCO_2$ at all pressures. The decrease in singlet lifetime (τ_f) of 2-naphthol in the presence of amine is consistent with a dynamic quenching mechanisms. In the case of MP, emission of 2-naphtholate is not observed and τ_f does not change with amine concentration, indicating the formation of a complex in the ground state, with the concomitant static deactivation of the 2-naphthol.

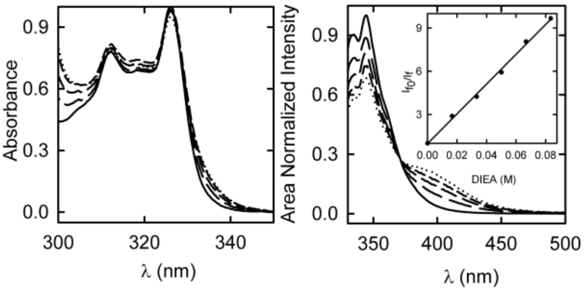


Figure 1.-Left : Absorption spectra of 2-naphthol with increasing amounts of DIEA in $scCO_2$ at constant density (16 mol/dm^3) and temperature (35 ºC). Concentration of amine varies from 0.017 to 0.100 M. Right: Area normalized corrected emission spectra (λ_{exc}=312 nm) for the same sample; inset: Stern-Volmer plot (K_{SV}=103 M^{-1}).

We found that, for all systems 2-naphthol/amine, fluorescence excitation spectra recorded at the emission wavelength of 2-naphthol and 2-naphtholate are coincident, thus proving that 2-naphtholate builds up in the excited state, and further emits.

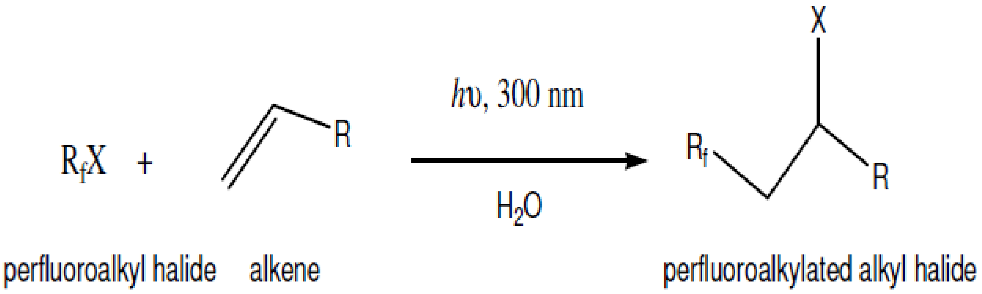
Light-initiated Perfluoroalkylation Reactions of Alkenes in water

Mariel Pamela Slodowicz,[1] **Al Postigo**[1]
[1]*Faculty of Science, University of Belgrano. Villanueva 1324 CP 1428-Buenos Aires, Argentina. alberto.postigo@ub.edu.ar* [1]

Perfluoroalkyl-substituted compounds are regarded as important components of fluorophors and for the introduction of fluorous tags into organic substrates. Their syntheses in organic solvents are achieved through different methods, among which, the addition of perfluoroalkyl radicals to unsaturated bonds represents a convenient choice. On the other hand, intermolecular radical reactions in water have attracted the attention of synthetic chemists as a strategic route to carbon-carbon bond formation reactions.
In previous works[1] we have reported the radical perfluoroalkylation reaction of alkenes mediated by silyl radicals, and obtained perfluoroalkyl-substituted compounds in fairly good yields. The radical triggering events employed consist of the thermal decomposition of an azo compound and the dioxygen initiation. Our results indicate that for intermolecular carbon-carbon bond formation reactions mediated by $(Me_3Si)_3SiH$, the decomposition of the azo compound 1,10- azobis(cyclohexanecarbonitrile) (ACCN) is the best radical initiator.

In this work we undertook the intermolecular addition of perfluoroalkyl radicals on electron rich alkenes and alkenes with electron withdrawing groups in water, initiated photochemically. The lack of hydrogen donor (*i.e.*: $(Me_3Si)_3SiH$) in our reaction medium facilitates a Halogen Atom Transfer reaction (HAT), affording the respective perfluoroalkylated alkyl halide in good yields. We also found that water exerts a relevant solvent effect on the rates of perfluoroalkyl radical additions onto double bonds.

Our account provides a versatile and convenient method to achieve perfluoroalkylation reactions of alkenes in water to render perfluoroalkylated haloalkanes as key intermediates in the synthesis of fluorophors and other fluorinated materials. This is the first report where perfluoroalkyl-substituted alkanes are synthesized through intermolecular radical carbon-carbon bond formation reactions in water, induced by light.

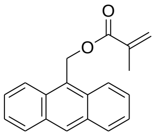


[1] Barata-Vallejo, Sebastián; Postigo, Al. "$(Me_3Si)_3SiH$-Mediated Intermolecular Radical Perfluoroalkylation Reactions of Olefins in Water". *J.Org.Chem.* **2010**, *75*, 6141-6148.

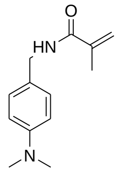
Photoinduced Electron Transfer Processes in Polymeric Nanoparticles

Claudia A. Solis, Hernán H. Montejano and Carlos A. Chesta
Departamento de Química, Universidad Nacional de Río Cuarto, (5800)-Río Cuarto, Argentina

The study of fast reactions involving radical pairs of low molecular weight (neutral or ionic) in polymer matrices is of great importance in understanding the mechanisms of the mechanical, thermal or photoinduced degradation of synthetic polymers. Likewise, understanding the phenomenon of charge transport through in solid matrices has been of large importance in the development of photoconductive polymers and in the design of optoelectronic devices. We present here preliminary studies on photoinduced electron transfer processes occurring in nanoparticulate polymeric matrices. Two different types of nanoparticles were synthesized copolymerizing: methyl methacrylate (MMA), ethylen eglycol dimethacrylate (EGDMA), (1) and (2); the last monomer especially synthesized for this study.



(1)



(2)

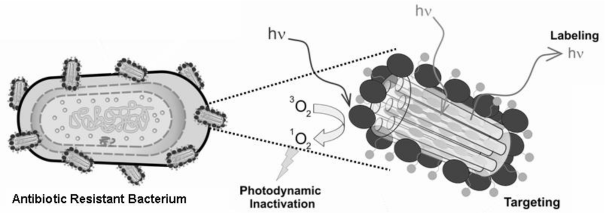
Syntheses were carried-out *via* the microemulsion polymerization technique (SDS micelles) and using the following monomer (molar) concentration ratios of (1) / (2) / MMA / EGDMA; nanoparticles type *a*: 1: 30: 80: 60 and type b: 1:0:110:60. This is, nanoparticles type *b* do not contain the electron donor monomer (2). The nanobeads were purified and characterized by light scattering and SEM microscopy. The estimated particles diameters are (10±6) nm. The particles are readily dispersible in organic solvents (acetonitrile, dichloromethane, etc.). The average number of fluorophores (1) in the particles is around 1.4. The fact that (1) is covalently linked to the polymers was verified by (excitation) fluorescence anisotropy experiments.

The fluorescence spectra (exciting the anthracenyl group at 350 nm) of both types of particles are identical. However, the florescence quantum yield of particles *b* is ~ 8 time larger than that observed for nanoparticles *a*. The decay time profiles measured (λ_{exc} = 350 nm) show for both type of particles a complex behavior. However, they are very similar and from their analysis it is concluded that there are two populations of fluorophores (1) in the polymeric matrices, one characterized by a $\tau \sim 5$ ns and the second by a $\tau \sim 17$ ns. The fluoresce spectrum obtained for particles *a* exciting at 310 nm (aromatic amine chromophore) shows the emission of the amine but also that of the anthracene. The results above suggest that the decreased fluorescence quantum yield observed for type *a* particles is due to a fast electron transfer reaction between the anthracene singlet excited state and amino groups in close contact. The fluorescence quenching of particles *b* by N,N-dimethylaniline in acetonitrile solutions was also studied. The Stern-Volmer plots obtained using stationary and dynamic (TCSPC) techniques do not agree. The analysis of the quenching data was carried out using a (modified) model proposed by J. N. Demas et. al. It is concluded that the short lifetime (1) population is quenched at rates similar to the observed in fluid media, while the long time living excited states are quenched ~ 100 times slower. The electron transfer nature of the quenching process was confirmed by (µsec) laser flash photolysis experiments. In the short time scale the transient spectra show absorptions that correspond to the anthracene anion and DMA cation radical.

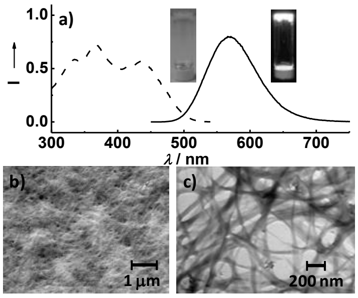
To aggregate or not to aggregate: that is the question

Cristian A. Strassert
Physikalisches Institut and Center for Nanotechnology (CeNTech)
Westfaelische Wilhelms-Universitaet Muenster
Heisenbergstrasse 11, D-48149 Muenster (Germany)
E-mail: ca.s@uni-muenster.de

Aggregation of planar chromophores greatly affects their photophysical performance. Phthalocyanine derivatives tend to form inactive dimers or oligomers, while Pt(II) complexes can show efficient emission from the MMLCT triplet state. It is possible to avoid the aggregation of phthalocyaninates by axially binding them to the surface of aluminosilicates. We have recently designed a multifunctional zeolite L-based hybrid material able to target, label and photoinactivate pathogenic and antibiotic resistant bacteria. A highly green luminescent dye was inserted into the channels of zeolite L nanocrystals for imaging and labeling the cells. The outer surface was functionalized with a Si(IV) phthalocyanine derivative that forms toxic singlet oxygen upon red light irradiation, and with amino groups for targeting the living microorganisms [1].



On the other hand, we recently developed a straightforward one-pot synthesis of neutral, soluble Pt(II) coordination compounds bearing a dianionic tridentate, terpyridine-like ligand. The emission intensity of the complex reached up to 87% PLQY in thin films, with concentration independent colour and efficiency. Consequently, we demonstrated its suitability as a dopant in solution processed OLEDs. Furthermore, we discovered that this complex is also able to self-assemble to bright nanofibers, which can interlock to yield highly emissive gels (90% PLQY), thus constituting a versatile building block for luminescent architectures. Therefore, it is possible to obtain two different materials starting from one single molecular entity, and monitor the self-assembly process with high sensitivity by the turn-on of the emission upon aggregation. The unique photophysical properties of the bright emitter arise from aggregation, as evidenced by the excitation and emission spectra, as well as excited state lifetimes [2].



[1] Strassert, C. A.; Otter, M.; Albuquerque, R. Q.; Höne, A.; Vida, Y.; Maier, B.; De Cola, L. *Angew. Chem. Int. Ed.* **2009,** *48*, 7928–7931.

[2] Strassert, C. A.; Chien, C.-H.; Galvez-Lopez, M. D.; Kourkoulos, D.; Hertel, D.; Meerholz, K.; De Cola, L. *Angew. Chem. Int. Ed.* **2011,** *50*, 946–950.

Effect of the complexation with cucurbit[6]uril on the spectroscopic properties of 1-aminopyrene

Valeria N. Sueldo Occello, **Alicia V. Veglia**
Instituto de Investigaciones en Físico Química de Córdoba (INFIQC); Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina, e-mail: aveglia@fcq.unc.edu.ar

Cucurbit[6]uril (CB6) is a macrocyclic host molecule comprised of six glycoluril units bridged by methylene groups defining a highly rigid and symmetric structure. The inner surface of the cavity is hydrophobic, whereas both portals are identical and surrounded by carbonyl groups permitting ion-dipole or hydrogen bond interactions. Many organic molecules have shown changes in their spectroscopic properties due the formation of supramolecular species with CB6.

In this work, the effect of the addition of the macrocycle on the photophysical properties of 1-aminopyrene was studied in HCOOH 55 % for the CB6 solubilization.

In aqueous solution 1-aminopyrene exists in two prototropic forms: the neutral specie, 1-$PYRNH_2$, and the protonated form, 1-$PYRNH_3^+$ (pK_a = 3,6). In the presence of CB6, the UV-Visible absorption spectrum of 1-$PYRNH_3^+$ exhibits a bathochromic shift (5 nm) and the absorbance decreases suggesting an interaction between this organic compound and the macrocycle. The value of the association constant determined in HCOOH 55 % w/v at 25.0ºC was $K_A = (2.5 \pm 0.2) \times 10^2\ M^{-1}$. The guest-host 1:1 stoichiometry was confirmed by the linear double reciprocal plot.

The fluorescence emission spectrum of a solution of 1-$PYRNH_3^+$ in HCOOH 55 % w/v shows a dual fluorescent behaviour: a strong fluorescence band centered at 440 nm attributed to the basic form and a weak band at $\lambda_{em} < 410$ nm related to the acidic specie. This effect is associated to the difference between the pK_a values of the ground and excited states (pK_a (1-$PYRNH_3^+$) > pK_a* (1-$PYRNH_3^+$)). The pK_a value of the excited state estimated from the Förster cycle was pK_a* = - 2.0. The short wavelength band enhances gradually upon successive addition of CB6, whereas the long wavelength fluorescence band shows a considerable decrease with increasing CB6 concentration. A global constant, that involves association and acid dissociation constants, was determined from the fluorescent data, $K_A = (14 \pm 1) \times 10^2\ M^{-1}$ (HCOOH 55 % w/v at 25.0ºC).

Therefore, the complexation between 1-$PYRNH_3^+$ and the macrocycle reduces its acidity in the excited state (pK_a* (1-$PYRNH_3^+$-CB6) > pK_a* (1-$PYRNH_3^+$)), resulting in the significant decrease of the emission of the neutral excited state and the enhancement of the emission from the protonated excited state.

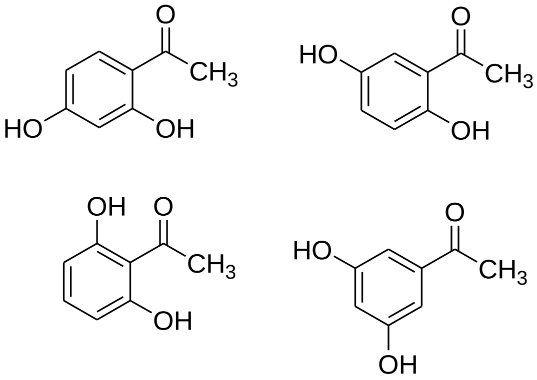
Photochemistry and Photophysics of several hydroxyacetophenones, potential UV-MALDI-MS matrices for carbohydrates

Luciano H. Di Stefano, Olga I. Tarzi, Rosa Erra-Balsells
CIHIDECAR- CONICET, Depto. de Química Orgánica, FCEN- Universidad de Buenos Aires Pab.2, Ciudad Universitaria, 1428 Buenos Aires, Argentina. E-mail: oitarzi@qo.fcen.uba.ar

One of the most succesful applications of organic photochemistry in solid state is UV-MALDI mass spectrometry. In this analytical technique, desorption/ionization of the analyte is induced by a UV laser and assisted by a photosensitizer (matrix).

Although the standard compounds used as matrices in UV-MALDI-MS are commercial, most of their photochemical properties remain unknown and there is not yet a clear model for the photosensitized process that takes place from the matrix to the analyte, after the UV-laser shot. Besides, there are no rules when it comes to choosing the right matrix for a particular analyte. Knowing which properties photosensitizers should have to efficiently desorb the analyte, could help not only to simplify the UV-MALDI experiment but also to obtain new structures useful as matrices. It is well known that commercial 2,4,6-trihydroxyacetophenone (THA) and 2,5-dihydroxybenzoic acid (gentisic acid) are good matrices especially for carbohydrates. Previous results in our laboratory showed photochemical stability and low fluorescence quantum yields for both compounds. Therefore, we decided to study several hydroxyacetophenones (scheme 1) to see how their photochemical and photophysical behaviour relates to their performance as UV-MALDI matrices.

UV-MALDI-MS experiments with different oligosaccharides showed that 2,5-dihydroxyacetophenone desorbed more efficiently the analyte than the other isomers tested. Electronic absorption, emission and excitation spectra of the compounds shown in the scheme were obtained and studies of their photochemical behaviour were performed in solution at different wavelengths and conditions. Thermal stability studies of these compounds in solid state were also conducted.



Scheme 1. Hydroxyacetophenones studied

The study of chemical reactions of excited pterin coenzymes in relation to photobiological functions

Taisiya A.Telegina, **Tamara A. Lyudnikova, Yulia L.Vechtomova, Andrey A. Buglak, Mikhail S. Kritsky**
A.N.Bach Institute of Biochemistry RAS, Moscow, 119071, Russia; telegina@inbi.ras.ru

Pterins act in organisms as coenzymes of essential biocatalytic reactions. Their molecules absorb ultraviolet, including UV-A photons. A detailed answer to the question of how light affects the pterins' chemical properties is important for understanding of their role as molecular targets of UV-light in organism and the possibility of participating in photocycles in photoreceptor proteins.

We have investigated the photochemical reactions of pterins belonging to two coenzyme families: tetrahydrobiopterin (H_4Bpt) and tetrahydrofolic acid (THFA), in the latter group the MTHF molecule has attracted particular attention. Irradiation of pterin solutions was carried out with the Xe-lamp with monochromator. Identification of the reaction products was based on HPLC separation, using photometric, fluorometric and amperometric detection of eluted compounds in combination with the analysis of their absorption and fluorescence spectra. At pH values below 2.5, H_4Bpt was resistant to oxidation by O_2 and UV-irradiation had no effect on its rate. The elevation of pH value above 2.5 dramatically accelerated the oxidation and within pH range from 4 to 10 its rate stayed constant. The oxidation of H_4Bpt led to the formation of H_2Bpt, but, in parallel, a cleavage of a side-chain from the C6 atom of pterin cycle and the H_2Pt formation took place with a further formation of products (biopterin, pterin, xanthopterin, etc.) which arose from oxidation of both H_2Bpt and dihydropterin. Irradiation led to a four-fold increase of the oxidation rate and expansion of a set of reaction products. Excitation of folic acid and biopterin in deaerated solution in the presence of electron donor resulted in their reduction to dihydro- and, further, tetrahydroforms. The involvement of quinonoid molecules in light-induced transformation of reduced pterins in solution requires further clarification. Although the transformation of excited pterin molecules could serve as a basis for the photochemical cycles in photoreceptor proteins, their participation in such cycles is unlikely due to the fact that the absorption bands of reduced forms are shifted to non-physiological UV-B wavelengths, and absorptivity of oxidized molecules is too low.

Of particular interest is to identify the properties by which a coenzyme 5,10-methenyltetrahydrofolate (MTHF) was selected to act as an antenna in DNA photolyases and cryptochromes. Investigation of the influence of UV-radiation on the reduced molecules of folate coenzymes showed that MTHF was extremely resistant to the damaging effect of light, and the presence of O_2, paradoxically, increased this resistance. Photodegradation of MTHF in presence of O_2 it led to the emergence of 10-formyl-folic acid, whereas in its absence the first identified product was THFA. Analysis of the properties of MTHF, a one-carbon group carrier in "dark" metabolism, allows speculating on why this molecule acts as an antenna in photoreceptor proteins. The presence of positively charged imidazoline cycle and the microenvironment ensuring its stability condition a unique combination in its molecule of high photon absorptivity in the physiological region of the spectrum with a resistance to photolysis, especially in O_2-containing environment. We believe that these details of the structure have determined an advantage of MTHF in the selection to the role of light-harvesting antenna in photoreceptors in a strictly aerobic branch of organisms' evolution.

Supported by Basic Research Program N^o 18 of the Presidium of Russian Academy of Sciences and by grant 11-04-01007-a of the Russian Foundation for Basic Research.

Synthesis of Functionalized Organic Dyes for Water Oxidation Catalysis

John J. Tomlin, **Smitha Pillai, Benjamin D. Sherman, Devens Gust, Thomas A. Moore, Ana L. Moore.**
Center for Bio-Inspired Solar Fuel Production and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604, USA.

As fossil fuels are depleted, the importance of securing alternative clean energy sources has become increasingly vital, and therefore many systems have been designed toward this end. Conventional systems such as wind power and silicon solar cells show promise, but both are prohibitively expensive on a large scale and have a limited maintenance free life time. One of the goals of our lab's research is to mimic photosynthesis, using light to split water into oxygen and hydrogen to provide a clean source of fuel.

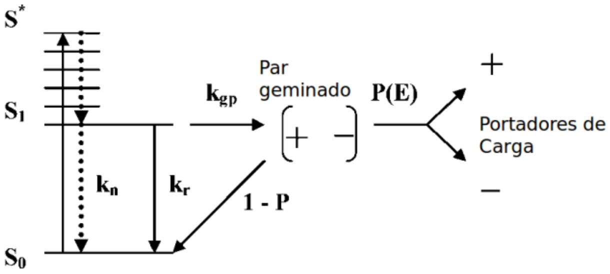
Most of the work has been on the synthesis of dyes for photocatalytic water oxidation. These dyes consist of a tetraphenylporphyrin functionalized with two phosphonate groups for preferentially binding to a tin oxide semiconductor surface, and two malonate groups for connecting the porphyrin to an iridium oxide nanoparticle catalyst.

In addition to the dyes for water oxidation, work on the synthesis of functionalized perylenes for use in the study of electron transfer from a dye into a semiconductor nanoparticle is being pursued. These studies are being done on single dye sensitized nanoparticles, using single molecule spectroelectrochemistry to probe the redox states of the sensitizer, while controlling the occupancy of the semiconductor's energy levels. These perylenes are attached to the nanoparticle using either phosphonate or carboxylate groups.

Theoretical Design And Energy Gap of Azo-Pyrrol Derivatives As Organic Photoconductor Materials

Ádincson Velásquez, **Cristina Valencia**
Grupo de Síntesis, Reactividad y Transformación de Compuestos Orgánicos, Escuela de Química, Universidad Nacional de Colombia, Medellín, Colombia.

Organic photoconductors materials were synthesized size 1960's used in laser printer and photocopiers machine as charge generation materials in multilayers photoconductors devices. Across big compounds used in this application, azo compounds were studied because their great charge generation quantum efficiency and the possibility to generate charge intrinsically and sensitized by charge transport materials in the interface. Electronic relocation in heterocyclic aromatic compounds had been studied in organic semiconductor materials for organic electronics.



We have undertaken DFT and TDDFT calculation to analysing Frontier Molecular Orbitals (FMO) for design new organic compounds capable to be organic photoconductors in solid state. The simulations were done in Quantum Espresso and Gamess and visualization of FMO were obtained by free software under GPL license. The Energy Gap was analysed in ground and excited state looking the probability transition in molecular orbitals to enhance electronic relocation by functional groups obtaining lower Band Gap materials.

The authors are grateful for the financial support of Universidad Nacional de Colombia, DIME project 20101008123, Dirección de Laboratorios, Facultad de Ciencias and Facultad de Minas for result socialization.

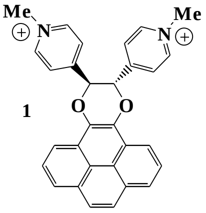
A Pyrene Dihydrodioxin with Pyridinium “Arms”: A Photochemically Activated DNA Cleaving Agent with Unusual Duplex Stabilizing Properties

Alexei Shamaev, Phillip A. Boda, Emil Khisamutdinov, Neocles B. Leontis, R. Marshall Wilson

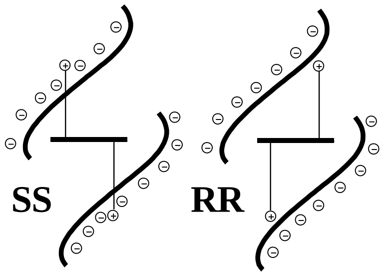
Department of Chemistry and The Center for Photochemical Sciences Bowling Green State University. Bowling Green, OH 43403

Dihydrodioxins (DHDs) of polycyclic aromatic hydrocarbons are known to intercalate into DNA and RNA. These dioxins serve as masking reagents for *ortho*-quinones, which they release upon irradiation. This quinone release process is known to proceed through the dihydrodioxin radical cation, which is strongly quenched when the DHD is intercalated within a DNA base-pair stack. Consequently, even though DHDs intercalate in DNA, and photochemically release *ortho*-quinones which cleave the DNA, this general strategy for DNA cleavage suffers from very low quantum yields. In an effort to rectify this problem, DHDs such as **1** have been prepared and found to undergo quinone release without significant quenching when intercalated in DNA. Thus, not only do the pyridinium “arms” serve as electron sinks that facilitate quinone release, but they also greatly facilitate the binding of the DHD to DNA via electrostatic attraction to the negatively charged phosphate backbone of duplex DNA.

The enantiomers of **1** have been resolved, and the pure enantiomers bind to DNA significantly enhancing the stability of the duplex (Fig. 1). Photochemical studies have shown localized damage occurs at the DHD binding sites. This damage involves both strand cleavage and base damage, and does not seem to involve sites remote from the binding sites that results from electron transfer through the base-pair stack. The results of these studies will be described in detail.



1



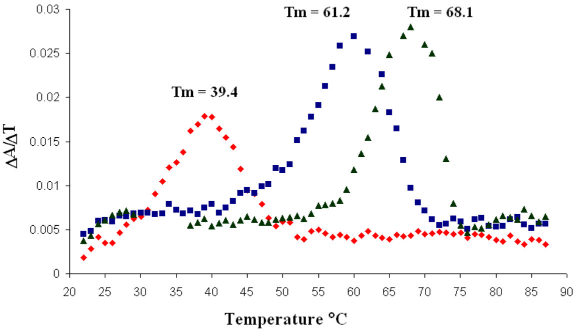


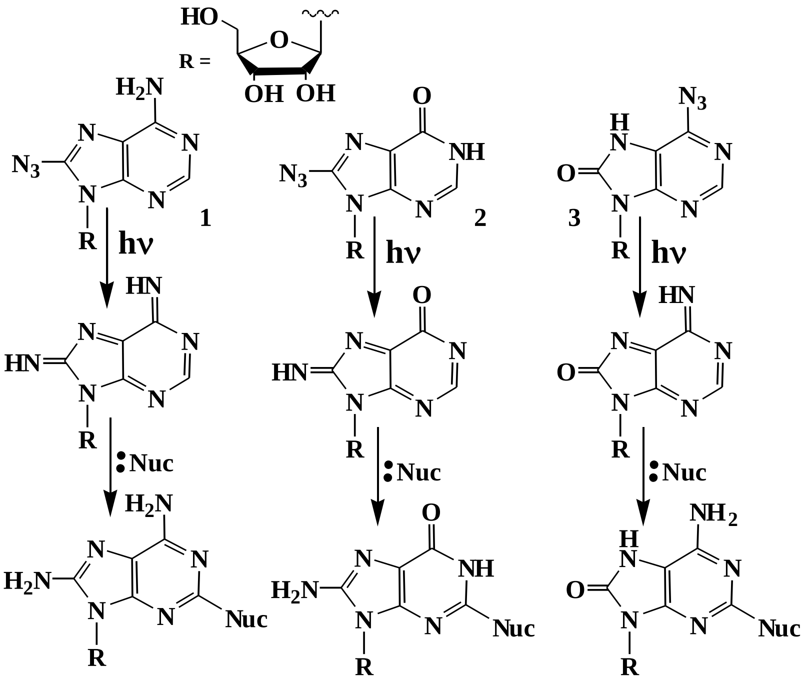
Figure 1. Differential melting plot for dodecamic duplex DNA (5’-GTTAGTATATGG-3’/3’-CAATCATATACC-5’) by itself (39.4°C), bound to a single molecule of one enantiomer of **1** (61.2°C), and to a single molecule of the second enantiomer of **1** (68.1°C).

A Transient Spectroscopic Study of the Photochemistry of Purine Azides

Denis Nilov, Max Panov, Kanykey Eilbayevna, Alexander N. Tarnovsky, and R. Marshall Wilson

Department of Chemistry and Center for Photochemical Sciences. Bowling Green State University. Bowling Green, Ohio 43403

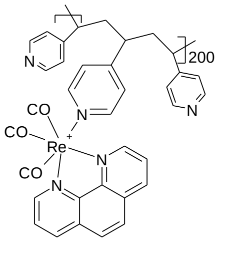
Azidopurines substituted in the 8-position undergo rapid, pH dependent loss of nitrogen upon irradiation to form purine iminoquinones, which in turn undergo Michael addition with a wide variety of nucleophiles at the 2-position. Reactive intermediates of this type are particularly intriguing since they may play a significant role in oxidative damage to nucleic acids. In order to better understand the mechanisms of iminoquinone formation and the reactions of these species with nucleophiles, an extensive transient spectroscopic study has been undertaken. Thus, the photochemistry of azides **1**-**3** has been examined from the femtosecond to the microsecond time domains. In general, these studies indicate that the quinoidal intermediates form rapidly within the picosecond time domain, and that attack by nucleophiles proceeds relatively slowly within the microsecond time domain. These results will be discussed in detail.



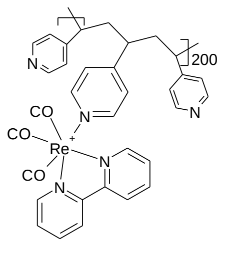
Protonation and Cu^{II} coordination effects on the luminescence of a Re^{I} polymer

Ulises N. Fagioli, Ezequiel Wolcan
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA, UNLP, CCT La Plata-CONICET), Diag. 113 y 64, Sucursal 4, C.C. 16, 1900 La Plata, Argentina
E-mail: ewolcan@inifta.unlp.edu.ar

Numerous studies have been concerned with thermal and photochemical reactions of inorganic polymers in the solid-state and solution phase. Interest in their photochemical and photophysical properties is driven by their potential applications in catalysis and optical devices.[1] The properties in the solution phase of the polymers **I** and **II** (see Scheme 1) were investigated in previous works.[1-3]



I



II

Marked differences were found between the photochemical and photophysical properties of polymers **I** and **II** and those of the related monomeric complexes, $pyRe^{I}(CO)_3L^+$ (py = pyridine; L = phen, 2,2′-bpy). The main cause of these differences is the photogeneration of MLCT excited states in concentrations that are much larger when $-Re^{I}(CO)_3L^+$ chromophores are bound to poly-4-vinylpyridine, $(vpy)_{600}$. This is the photophysical result of Re^{I} chromophores being crowded in strands of a polymer instead of being homogeneously distributed through solutions of a $pyRe^{I}(CO)_3L^+$ complex.

Coordination of Cu^{II} ions to poly-4-vinylpyridine has been reported in the literature.[4-8] In this presentation, we report the coordination of Cu^{II} (X = Cl or CF_3SO_3) species to $\{[(vpy)_2\text{-}vpyRe(CO)_3phen]CF_3SO_3\}_{n=200}$ and its effect on the polymer luminescence. We also explore the effect of protonation of the free pyridines of the polymer backbone on the Re^{I} polymer's luminescence.

The addition of an acetonitrile solution of CuX_2 (X = Cl or CF_3SO_3) to an acetonitrile solution of the polymer **I** produces a rapid coordination of the Cu^{II} species to the uncoordinated pyridines with approximate stoichometry of $[Cu^{II}]/[py] \approx 0.4$ and $[Cu^{II}]/[py] \approx 0.2$ for $CuCl_2$ y $Cu(CF_3SO_3)_2$, respectively. The emission spectrum of $\{[(vpy)_2\text{-}vpyRe(CO)_3phen]CF_3SO_3\}_{n=200}$ in deoxygenated CH_3CN at room temperature exhibited an unstructured band centered at 550 nm. The quenching of the luminescence of the Re^{I} polymer by $CuCl_2$ and/or $Cu(CF_3SO_3)_2$ was studied using steady state and time-resolved techniques under similar experimental conditions to those utilized in the investigation of the binding of Cu^{II} species to the Re^{I} polyelectrolyte. The MLCT luminescence quenching by Cu^{II} species does not follow a Stern-Volmer kinetics. Moreover, there is a progressive shifting of the emission spectrum maximum to shorter wavelengths as the quenching proceeds.

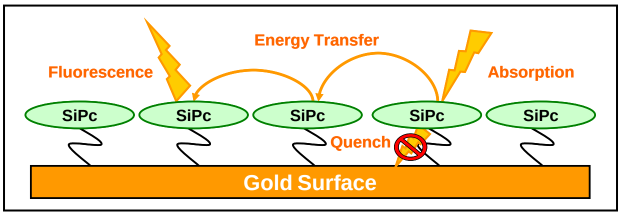
REFERENCES

[1] Wolcan, E.; Ferraudi, G. *J. Phys. Chem. A* **2000**, *104*, 9281.
[2] Wolcan, E.; Feliz, M. R. *Photochem. Photobiol. Sci.* **2003**, *2*, 412.
[3] Wolcan, E.; Alessandrini, J. L.; Feliz, M. R. *J. Phys. Chem. B* **2005**, *109*, 22890.
[4] Tsuchida, E.; Kaneko, M.; Nishide, H. *Makromol. Chem.* **1973**,*164*, 203.
[5] Kirsh, Y. E.; Kovner, V. Ya.; Kokorin, A. I.; Zamaraev, K. I.;Cherniak, V. Ya.; Kabanov, V. A. *Eur. Polym. J.* **1974**, *10*, 671.
[6] Agnew, H. *J. Polym. Sci.* **1976**, *14*, 2819.
[7] Nishide, H.; Tsuchida, E. *J. Polym. Sci.* **1981**, *19*, 835.[8] Jeschke, G. *J. Phys. Chem. B* **2000**, *104*, 8382.

Synthesis and Attachment of Thiol-Functionalized Silicon(IV) Octabutoxy-Phthalocyanine and Porphyrin to Gold Surfaces as Artificial Antennas

Katherine L. Wong[1], **Jesse Bergkamp**[1], **Gerdenis Kodis**[1], **Ana. L. Moore**[1], **Tom A. Moore**[1]

Department of Biochemistry & Chemistry, Arizona State University, Tempe, Arizona 85287, USA[1]



This project seeks to produce an artificial antenna system along a gold surface to better understand the structure and function for solar energy harvesting in purple photosynthetic bacteria. Current literature reports several phthalocyanine dyes placed on a 2D surface in different orientations depending on the geometry of the linker and placement of the thiol group, however their photophysical properties were not studied[1, 2]. This poster presents the synthesis of three different silicon(IV)-1,4,8,11,15,22,25-octabutoxyphthalocyanine (**SiPc**) dyes with protected thiols connected through a phenyl ring at the axial positions of a central Si(IV) atom. Combinations of ether or ester bonds connecting the linker and the silicon atom, and acetyl or methyl protected thiols were synthesized to determine the best way to form a SiPc self-assembling monolayer on a gold surface without quenching the fluorescence of the tetrapyrrole. In addition, 5-(4-methylmercaptophenyl)-10,15,20-trimesitylporphyrin was synthesized as a model for a perpendicular orientation of a dye on the gold surface. This project is involved in the development of a method, based on changes in the steady state absorption and fluorescence and fluorescence lifetimes, to determine whether the dyes are attached to the surface of unprotected gold nanoparticles and to what extent their fluorescence is quenched. These observations will guide the construction of dyes with the required linkages to be used for attachment to gold surfaces minimizing non-radiative loses.

1. Li, Z.; Lieberman, M.; Hill, W., XPS and SERS Study of Silicon Phthalocyanine Monolayers: Umbrella vs Octopus Design Strategies for Formation of Oriented SAMs. *Langmuir* **2001,** 17, (16), 4887-4894.
2. Revell, D. J.; Chambrier, I.; Cook, M. J.; Russell, D. A., Formation and spectroscopic characterisation of self-assembled phthalocyanine monolayers. *Journal of Materials Chemistry* **2000,** 10, (1), 31-37.

PHOTO-AUTOIONIZATION STRUCTURE IN THE HALOGEN SYSTEMS: Br_2, I_2, BrCl, ICl and IBr

Andrew J. Yencha[*] **and Devinder Kaur**[#]
Department of Chemistry, State University of New York at Albany, Albany, New York 12222, USA

The photochemical utility of diatomic halogen and interhalogen molecules in flash photolysis studies for the photodissociative production of excited and ground state halogen atoms have been known for a long time. More recently diatomic halogen and interhalogen molecules have received considerable attention due to the reactivity of their excited states, particularly with rare gas atoms related to excimer laser-light generation.

We have recorded both the photoionization yield spectra and the ion-pair photodissociative excitation function spectra in the vicinity of the ionization limits of the molecules Br_2, I_2, BrCl, ICl and IBr using synchrotron radiation on beamline U11 at the National Synchrotron Light Source facility. We analyzed these in terms of their formation mechanisms where we found a strong correlation between these two types of spectra. We report here on the autoionizing structure in the photoionization yield spectra of these molecules, having previously published our analyses of the ion-pair formation excitation function spectra for the same molecules [1-3].

As typical examples of the ion-yield spectra we obtained, we present in Fig. 1 the ion-yield spectrum of Br_2^+ and in Fig. 2 the ion-yield spectrum of IBr^+ in comparison with the respective calculated autoionization functions for the molecules. In the case of Br_2^+ formation, the calculated autoinization function was derived from the summation of $np\pi$ Rydberg series for n=9-11 converging on the $X\ ^2\Pi_{g,1/2}$ state of Br_2^+. In the case of IBr^+ formation, the autoionizing structure in the ion-yield curve could be simulated by the overlapping of the Rydberg series $ns\sigma$ for n=9-14 converging on the $X\ ^2\Pi_{1/2}$ state of IBr^+. These analyses were greatly assisted by the Rydberg series found to be present in the ion-pair photodissociative excitation function for the respective molecule that occurs at an energy just below the ionization threshold of the molecule [1-3].

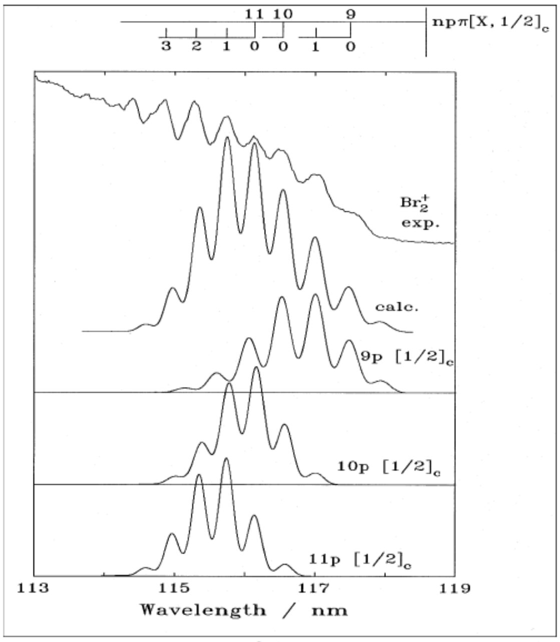


Fig. 1. A comparison of the experimental ion-yield curve for Br_2^+ formation and calculated autoionization function of Br_2.

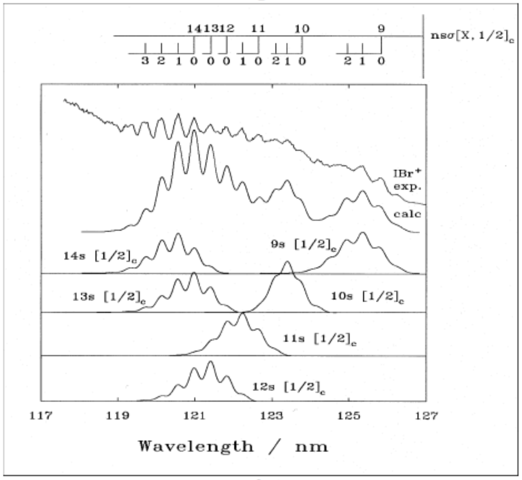


Fig. 2. A comparison of the experimental ion-yield curve for IBr^+ formation and calculated autoionization function for IBr.

References:

[1] A.J. Yencha et al., Chem. Phys. Lett. 165 (1990) 283.
[2] A. Kvaran et al., Chem. Phys. Lett. 179 (1991) 263.
[3] D. Kaur et al., Org. Mass Spectrom. 28 (1993) 327.

[*] E-mail address: yencha@albany.edu
[#] Permanent address: Rockwood Electronic Materials Singapore, 14 Tuas Avenue 20, Singapore 638826

INDEX

INDEX

INDEX

INDEX