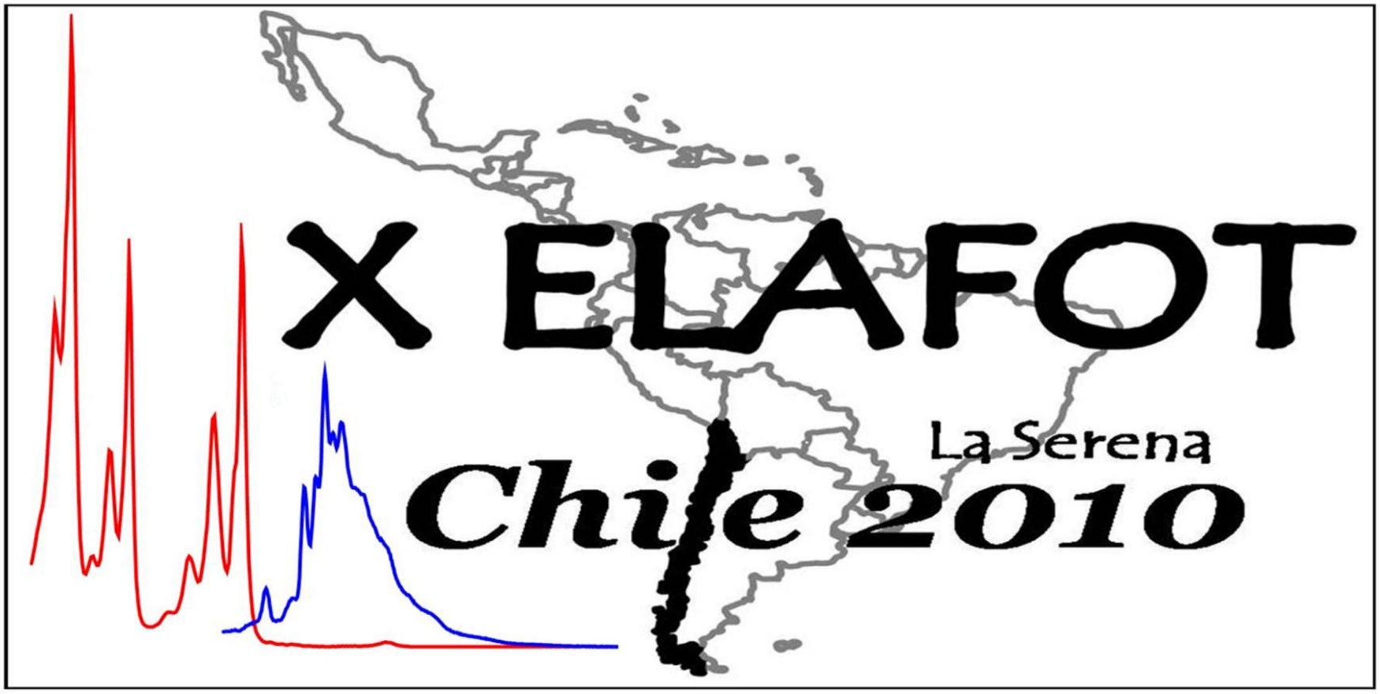


X ELAFOT

La Serena

Chile 2010

UNIVERSIDAD
ANDRES BELLO

X ENCUENTRO LATINOAMERICANO DE FOTOQUÍMICA Y FOTOBIOLOGÍA
OCTUBRE 10 – 14, 2010
LA SERENA, CHILE

FUNDINGS

MELVYN BECERRA Y CIA. LTDA

MERCK S.A. CHILE

NESTLÉ S.A. CHILE

LUZCHEM

SPONSORSHIP

UNIVERSIDAD DE SANTIAGO DE CHILE

UNIVERSIDAD DE CHILE

UNIVERSIDAD NACIONAL ANDRÉS BELLO

PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE

SOCIEDAD CHILENA DE QUÍMICA

INTER-AMERICAN PHOTOCHEMICAL SOCIETY

COMISIÓN NACIONAL DE INVESTIGACIÓN CIENTÍFICA Y TECNOLÓGICA

CONTENTS

Organizing Committee

Dra. Elsa Abuín Presidente	Universidad de Santiago de Chile
Dr. Antonio Zanocco Vice-Presidente	Universidad de Chile
Dr. Alexis Aspee	Universidad de Santiago de Chile
Dra. Nancy Pizarro	Universidad Nacional Andrés Bello
Dra. Else Lemp	Universidad de Chile
Dr. Marco Soto	Pontificia Universidad Católica de Chile
Dr. Julio de la Fuente	Universidad de Chile
Dr. Eduardo Silva	Pontificia Universidad Católica de Chile
Dr. Andrés Olea	Universidad Nacional Andrés Bello
Dr. Germán Günther	Universidad de Chile

Scientific Committee

Dr. Antonio Zanocco, Chile Presidente	Universidad de Chile
Dra. María Victoria Encinas, Chile	Universidad de Santiago de Chile
Dr. Eduardo Lissi, Chile	Universidad de Santiago de Chile
Dr. Pedro Aramendía, Argentina	Universidad de Buenos Aires
Dr. Carlos Previtali, Argentina	Universidad Nacional de Río Cuarto
Dra. Mónica González, Argentina	Universidad Nacional de La Plata
Dr. Jose Carlos Netto-Ferreira, Brasil	Universidade Federal Rural do Rio de Janeiro
Dr. Frank Quina, Brasil	Universidade de São Paulo
Dr. Mauricio Baptista, Brasil	Universidade de São Paulo

PROGRAM

SUNDAY, OCTOBER 10

16:00 – 20:00	**Registration**
20:30 – 22:30	**Reception**

MONDAY, OCTOBER 11

8:20 – 9:00	**Welcome**	
Chairman	M. V. Encinas	
9:00 – 9:50	C1	A. Moore
9:50 –10:15	OC1	V. Barachevsky
10:15 – 10:40	OC2	B. Barja
10:40 – 11:05	Coffee Break	
11:05 – 11:55	C2	R. Nome
11:55 – 12:20	OC3	M. Krayushkin
12:20– 14:50	Lunch	
Chairman	M. C. González	
14:50 – 15:40	C3	T. Atvars
15:40 – 16:05	OC4	H.-M. Vieth
16:05 – 16:30	Coffee Break	
16:30 – 16:55	OC5	J.C. Netto-Ferreira
16:55 – 17:20	OC6	M. González-Béjar
17:20 – 17:45	OC7	M. A. Biasutti

TUESDAY, OCTOBER 12

Chairman	G. Günther	
8:35 – 9:25	C4	S. A. Sánchez
9:25 – 9:50	OC8	A. V. Yurkovskaya
9:50 –10:15	OC9	R. Palacios
10:15 – 10:40	OC10	Ch. Pavani
10:40 – 11:05	Coffee Break	
11:05 – 11:55	C5	P. Aramendia
11:55 – 12:20	OC11	C. Kawai
12:20– 14:50	Lunch	
Chairman	A. Aspée	
14:50 – 15:40	C6	A. Thomas

15:40 – 16:05	OC12	R. D. Falcone
16:05 – 19:00	Poster Session 1 (Odd numbers) Coffee	

WEDNESDAY, OCTOBER 13

Chairman M. Neumann

8:35 – 9:25	C7	G. Cosa
9:25 – 9:50	OC13	E. Lissi
9:50 –10:15	OC14	N. M. Correa
10:15 – 10:40	OC15	M.V. Encinas
10:40 – 11:05	Coffee Break	
11:05 – 11:55	C8	S. Braslavsky
11:55 – 12:20	OC16	
12:20– 14:50	Lunch	

Chairman E. Lissi

14:50 – 15:15	OC17	E.Alarcón
15:15 – 15:40	OC18	A.M.Edwards
15:40 – 16:05	OC19	F.H.Quina
16:05 – 19:00	Poster Session 2 (Even numbers) Coffee	

THURSDAY, OCTOBER 14

Chairman P. Aramendia

8:35 – 9:00	OC20	D. E. Weibel
9:00 – 9:25	OC21	M. J. Llansola-P.
9:25 – 9:50	OC22	G. Oksdath-M.
9:50 –10:15	OC23	M. C. González
10:15 – 10:40	OC24	M. P. Serrano
10:40 – 11:05	Coffee Break	
11:05 – 11:30	OC25	P. Cometto
11:30 – 11:55	OC26	D. Silva M.
11:55 – 12:20	OC27	M. Martin
12:20– 21:00	Lunch/City Tour/Free	
21:00	Dinner and Nice Party	

	Sunday,Oct. 10	Monday, Oct. 11		Tuesday, Oct. 12		Wednesday, Oct. 13		Thursday, Oct. 14	
8:20		**Welcome** (8:20-9:00)							
8:35 – 9:00				Chairman´s	Susana Sánchez	Chairman´s	Gonzalo Cosa	Chairman´s	D. E. Weibel
9:00 - 9:25		Chairman´s	Ana Moore	G. Günther		M. Neumann			M. J. Llansola-P.
9:25 - 9:50		M.V. Encinas			A.V.Yurkovskaya		E. Lissi		G. Oksdath-M.
9:50 -10:15			V. Barachevsky		R.Palacios		N. M. Correa		M.C.Gonzalez
10:15 -10:40			B. Barja		Ch. Pavani		M.V. Encinas		Mariana Serrano
10:40 -11:05			Coffee Break		Coffee Break		Coffee Break	P.Aramendia	Coffee Break
11:05 -11:30			René Nome		Pedro Aramendia		Silvia Braslavsky		P. Cometto
11:30 -11:55									D. Silva M.
11:55 -12:20			M. Krayushkin		Cintia Kawai		Short Talk16		M. Martin
12:20-14:50		**Lunch**		**Lunch**		**Lunch**		**Lunch/ City Tour/ Free**	
14:50-15:15		Chairman´s	Teresa Atvars	Chairman´s	Andrés Thomas	Chairman´s	E.Alarcón		
15:15 -15:40		Mónica C. González		A. Aspée		E. Lissi	A.M.Edwards		
15:40-16:05	**Registration** (16:00-20:00)		H.-M. Vieth		R. D. Falcone		F.H.Quina		
16:05- 16:30			Coffee Break	**Poster Session 1** Coffee		**Poster Session 2** Coffee			
16:30-16:55			J.C. Netto-Ferrei.						
16:55-17:20			M. González-B.						
17:20-17:45			M. A. Biasutti						
17:45-19:00									
20:30	**Reception**							21:00	Dinner and Nice Party

PLENARY CONFERENCES

C1

DESIGN OF PHOTOELECTROCHEMICAL CELLS FOR WATER SPLITTING AND FUEL PRODUCTION

Gary F. Moore,[*] Michael Hambourger,[*] Benjamin Sherman,[*] Smitha Pillai,[*] Jesse Bergkamp,[*] Ernesto Mariño-Ochoa,[#] Marcelo Videa,[#] Devens Gust,[*] Thomas A. Moore[*] and Ana L. Moore[*]

[*] Center for Bioenergy and Photosynthesis, Department of Chemistry and Biochemistry,
Arizona State University, Tempe, AZ, USA 85287-1604, amoore@asu.edu
[#] Departmento de Química, Tecnológico de Monterrey, Campus Monterrey, Monterrey, N.L.,
México 64849

Key words: photosynthesis, high-potential porphyrins, low-potential naphthalocyanines

The design of bioinspired schemes that couple solar energy conversion to the oxidation of water and the subsequent use of the reducing equivalents to synthesize energy-rich compounds, such as hydrogen or fuels based on reduced carbon is the main objective of our present research.[1] In order to establish the design principles for a tandem, two junction (or threshold) photochemical cell, we are assembling Grätzel-type photoelectrodes that model photosystems I and II (PSI and PSII) of plants. The photoanode model of PSII will contain a mimic of the donor side (water oxidizing side) of PSII reaction centers. In PSII, tyrosine Z (Tyr_Z) mediates charge transport between the photo-oxidized primary donor ($P680^{\bullet +}$) and the oxygen-evolving complex (OEC). The oxidation of Tyr_Z by $P680^{\bullet +}$ likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue (His190). This coupling of proton and redox chemistry is thought to poise the Tyr_Z oxidation potential between those of $P680^{\bullet +}$ and the OEC.

We have prepared a bioinspired system ($BiP\text{-}PF_{10}$) consisting of a high oxidation potential porphyrin (PF_{10}, 1.59 V vs. NHE, a model of P680) that is covalently attached to a benzimidazole-phenol pair (BiP) that mimics the Tyr_Z-His190 pair in PSII. Electrochemical studies show that the phenoxyl radical/phenol couple of the model system is chemically reversible with a midpoint potential of 1.24 V vs. NHE and is therefore thermodynamically capable of water oxidation. When the $BiP\text{-}PF_{10}$ construct is attached to TiO_2 nanoparticles and excited with visible light, it undergoes photoinduced electron transfer. Electrons are injected into the semiconductor and the corresponding holes are localized on either the porphyrin ($BiPPF_{10}^{\bullet +}\text{-}TiO_2^{\bullet -}$) or the phenol ($BiP^{\bullet +}\text{-}PF_{10}\text{-}TiO_2^{\bullet -}$). EPR provides a clear spectroscopic picture of these processes.[2] The photoelectrode model of PSI will be sensitized by low potential naphthalocyanines or phthalocyanines, which absorb light in the near IR region of the spectrum. Upon photoexcitation, these dyes are designed to inject electrons into semiconductors having sufficiently negative conduction bands to effectively drive the reduction of protons to hydrogen at a cathode. The semiconductor will be electrically wired to a cathode suitable for hydrogen production: either a metal electrode (Pt or Ni) or a hydrogenase-modified carbon electrode.[3]

1. Hambourger M. et al. *Chem. Soc. Rev*, 2009, *38*, 25–35.
2. Moore, G. F. et al. *J. Am. Chem. Soc*. 2008, *130*, 10466–10467.
3. Hambourger M. et al. *J. Am. Chem. Soc*. 2008, *130*, 2015–2022.

C2

ULTRAFAST SPECTROSCOPY APPLIED TO THE STUDY OF EXCITED STATE DYNAMICS IN COMPLEX SYSTEMS

René Nome

Universidade Estadual de Campinas, Instituto de Química,
Campinas, SP - Cep 13083-970, Brasil. e-mail: nome@iqm.unicamp.br

Keywords: ultrafast spectroscopy, protein-chromophore interactions, fluorescence

Protein-chromophore interactions in photoreceptors often shift the chromophore absorbance maximum to a biologically relevant spectral region. A fundamental question regarding such spectral tuning effects is how the electronic ground state S_0 and excited state S_1 are modified by the protein. It is widely assumed that changes in energy gap between S_0 and S_1 are the main factor in biological spectral tuning. We report a generally applicable approach to determine if a specific residue modulates the energy gap, or if it alters the equilibrium nuclear geometry or width of the energy surfaces. This approach uses the effects that changes in these three parameters have on the absorbance and fluorescence emission spectra of mutants. We apply this strategy to a set of mutants of PYP containing all 20 side chains at active residue 46. While the mutants exhibit significant variation in both the position and width of their absorbance spectra, the fluorescence emission spectra are largely unchanged. This provides strong evidence against a major role for changes in energy gap in the spectral tuning of these mutants and reveals a change in the width of the S_1 energy surface. We determined the excited state lifetime of selected mutants and the observed correlation between the fluorescence quantum yield and lifetime shows that the fluorescence spectra are representative of the energy surfaces of the mutants. These results reveal that residue 46 tunes the absorbance spectrum of PYP largely by modulating the width of the S_1 energy surface.

C3

FOTOFÍSICA E TRANSIÇÕES DE FASE EM FILMES FINOS DE POLÍMEROS CONJUGADOS

Teresa Dib Zambon Atvars* **e Raquel Aparecida Domingues**

* Departmento de Físico-Química, Instituto de Química, Universidade Estadual de Campinas, Campinas, Brazil, P.O. Box 6154, 13084-971, SP, Brazil, e-mail: tatvars@iqm.unicamp.br

Key Words: filmes finos, transições, polímeros conjugados

Entre as técnicas usadas na determinação de transição de fase está a espectroscopia de fluorescência, sendo que através desta técnica os processos de relaxação podem ser determinados através do acompanhamento da variação da intensidade de emissão com a variação de temperatura numa faixa de 20 a 420 K, e mudanças de inflexão na curva indicam transições de fase que ocorrem na amostra.

Quando são estudadas amostras de filmes finos, a técnica de fluorescência mostra-se bastante eficiente e quase única no estudo de transições de fase, uma vez que técnicas usuais como DSC e TGA não podem ser utilizadas em casos nos quais os filmes não são auto-sustentados.

Neste trabalho forma determinadas as temperaturas de transição de filmes finos de polímeros conjugados, incluindo os derivados de polifluorenos, através da técnica de espectroscopia de fluorescência. Os filmes foram depositados por spin coating e foi usado como substrato uma janela de quartzo. A espessura dos filmes foi similar às das camadas nos dispositivos eletroluminescentes e foi possível verificar que com o aumento de espessura as transições passam a ocorrer em temperaturas também maiores, mostrando assim um efeito de confinamento de nanoescala[1]. Este efeito pode ser entendido qualitativamente sabendo-se que as transições em polímeros está associada com a mobilidade segmentar cooperativa de dezenas a centenas de unidades de repetição e a presença de uma superfície localmente livre reduz essa cooperatividade, reduzindo assim a temperatura de transição de fase[2].

Uma mudança bastante pronunciada nos espectros de emissão de fluorescência também ocorre com o aumento de espessura dos filmes feitos com derivados de polifluorenos. Isso indica a ocorrência de alterações conformacionais do polímero quando confinados de diferentes maneiras, sugerindo também uma maior presença de agregados no caso de filmes mais finos.

1- R. D. Priestley, M. K. Mundra, M. J. Barnett, L. J. Broadbelt, J. M. Torkelson, Aust, J. Chem. 2007, 60, 765.
2- C. J. Ellison, J. M. Torkelson, Nat. Mat. 2003, 2, 695.

Agradecimentos: FAPESP, CNPq/INEO.

C4

LAURDAN GENERALIZED POLARIZATION MICROSCOPY FOR THE STUDY OF CELL MEMBRANE HETEROGENEITY

Susana A. Sánchez

Department of Biomedical Engineering, University of California at Irvine, Irvine, USA. Laboratory for Fluorescence Dynamics, 3208 Natural Sciences II, Irvine, CA 92697. susanas@uci.edu

Fluorescence techniques such as fluorescence lifetime or simple intensity measurements were originally developed to be used in a cuvette fluorometer. The implementation of these techniques in the microscope added to the measurements the spatial resolution needed for cellular studies but also forced researchers to change the experimental design and the analytical methods used. One of these techniques, Laurdan Generalized Polarization is presented here.

Laurdan (6-lauroyl,1-2-dimethylamino naphthalene) is a fluorescent dye designed and synthesized in 1979 by Gregorio Weber to study the phenomenon of dipolar relaxation. Polarity changes are detected by shifts in the Laurdan emission spectrum, and the Generalized Polarization function (GP) was defined as a way of measuring the wavelength displacements. Changes in GP values when Laurdan is within a lipid bilayers in either fluid or gel phase, extended the use of the technique to the field of membrane dynamics and protein-lipid interaction. In 1997 GP measurements were done for the first time in the microscope and two-photon excitation was required to minimize the photo bleaching of the dye. Several reports have been published specially in the field of visualization of membrane packing and lipid domains both *in vitro* and *in vivo*. In this talk we explain the basic concepts of the technique both in cuvette and in the microscope, and we present results using this technique to study the effect of the lipid phase on cholesterol removal *in vitro* and *in vivo.*

[1] G. Weber, F.J. Farris, Biochemistry. 18 (1979) 3075.
[2] T. Parasassi, G.D. Stasio, A. d'Ubaldo, E. Gratton, Biophys J. 57 (1990) 1179.

C5

NEAR FIELD FLUORESCENCE FLUCTUATION SPECTROSCOPY WITH GOLD NANOPARTICLES

Laura Estrada[1], Pedro F. Aramendía[2], and Oscar E. Martínez[1]

[1]Departamento de Física and [2]INQUIMAE, Dept. Química Inorgánica.
FCEN, Universidad de Buenos Aires, Buenos Aires, Argentina, Pabellón 2. C. Universitaria,
e-mail: pedro@qi.fcen.uba.ar

Keywords: Near field, fluorescence, fluctuation spectroscopy.

The interaction of chromophores with metal nanoparticles (MNPs) has been extensively studied in recent years. Fluorophores in the close vicinity of metal nanoparticles are interesting systems to develop sensors, especially in the fields of cellular tracking and imaging. Fluorescence enhancement of a fluorophore in the nanometer distance scale from a metal nanoparticle is well documented, a phenomenon attributed to the near field interaction of the molecule oscillating transition dipole with a characteristic resonance frequency of the free electrons of the nanostructure.

MNPs can modify the emission of fluorescent molecules by increasing the excitation and emission rates (plasmonic enhancement), as well as by modifying the non-radiative energy transfer from the molecule to the particle (quenching effect). These processes are influenced by the MNP size, shape, and material; the fluorophore absorption and emission properties, quantum yield, and orientation; MNP-fluorophore distance; and the dielectric constant of the surrounding medium. The modification in excitation, emission, and non-radiative energy transfer rates is distance dependent and, as a result, an overall fluorescence quenching results at very short distance from the MNP, an emission enhancement is observed at intermediate distances, and no influence results, for a molecule placed at a distance greater than about twice the MNP radius. It is clear that a careful analysis of the effects of the actual MNP-fluorophore characteristics on the fluorescence emission is of broad interest to find conditions that optimize a desirable property of the probe. For a rational design of a MNP-fluorophore hybrid system it is necessary to take into account all the variables that modify the chromophore photophysics and that can lead to the desired fluorescence enhancement.

We summarize a careful study on the influence of all the mentioned variables on the photophysics of molecules in the close vicinity to MNPs and we present results of three experiments using the emission enhancement by 40 nm radius AuNP irradiated in the green in a confocal microscope. 1) Fluorescence fluctuation spectroscopy that shows a reduction of a factor of 10^4 in the observation volume. 2) Localization experiments that show the detectability of Rose Bengal with a great contrast. 3) Tracking experiments in cells that show an increase in tracking time and persistence against photobleaching.

C6

OXIDATION OF BIOMOLECULES PHOTOSENSITIZED BY PTERINS AND LUMAZINES: MECHANISMS AND BIOMEDICAL IMPLICATIONS

M. Paula Denofrio,[*] Mariana Vignoni,[*] M. Laura Dántola,[*] Esther Oliveros,[#] Carolina Lorente[*] and Andrés H. Thomas[*]

* INIFTA, Departamento de Química, Facultad de Ciencias Exactas, UNLP, CCT-La Plata,
CONICET. Diagonal 113 y 64, (1900) La Plata, Argentina. E-mail: athomas@inifta.unlp.edu.ar
Laboratoire des IMRCP, UMR CNRS 5623, Université Paul Sabatier (Toulouse III), 118,
route de Narbonne, F-31062 Toulouse cédex 9, France.

Keywords: Pterins, lumazines, photosensitization.

Pterins and lumazines, heterocyclic compounds present in biological systems, play various roles ranging from pigments to enzymatic cofactors for numerous redox and one-carbon transfer reactions. Under UV-A excitation, these biomolecules generate reactive oxygen species, such as singlet oxygen, and are able to photoinduce DNA damage.[1] Moreover, their photodynamic activity has been demonstrated in HeLa cells.[2]

Studies carried out with purine nucleotides[2,3] or EDTA[4] as substrates and pterins or lumazines as sensitizers revealed a general experimental behavior. When an air-equilibrated solution containing a given substrate and a given sensitizer is exposed to UV-A irradiation, the concentrations of the substrate and O_2 decrease, production of H_2O_2 is observed and the concentration of the sensitizer remains constant. The photosensitized process is favored by superoxide dismutase, but inhibited in O_2-equilibrated solutions or by the presence of iodide. The mechanism proposed consists in a type I photooxidation that involves an initial electron transfer from the substrate (*e.g.*, a nucleotide) to the triplet excited state of the sensitizer. In the following step, the resulting radical anion reduces dissolved O_2 to form the superoxide anion and regenerate the sensitizer. Finally a group of processes, that include the reactions of the substrate radical cation and its deprotonated form with O_2 and H_2O, leads to the oxidation of the substrate.

Folic acid (PteGlu) and 7,8-dihydrobiopterin (H_2Bip) undergo photooxidation in air-equilibrated aqueous solution upon UV-A exposure to yield 6-formylpterin (Fop) and biopterin (Bip), respectively. Photodegradation of PteGlu is involved in depletion of serum folate levels caused by sunlight exposure, whereas photooxidation of H_2Bip is a potential source of Bip, a compound toxic for melanocytes, in the skin of patients suffering vitiligo. In both cases, the rate of the reactant (PteGlu or H_2Bip) degradation increases with irradiation time. Analysis of this “auto-photocatalytic” effect on the basis of the general mechanism proposed in the previous paragraph revealed[5] that the reactions consist in photosensitized processes in which the photoproduct (Fop or Bip) acts as a sensitizer of its own production. Again, the first step involves an electron transfer from the substrate to the triplet excited state of the sensitizer.

References

1 C. Lorente, A. H. Thomas, *Acc. Chem. Res.*, 2006, **39**, 395.
2 M. P. Denofrio *et al.*, *Photochem. Photobiol. Sci.*, 2009, **8**, 1539.
3 G. Petroselli *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 3001.
4 M. L. Dántola *et al.*, *Free Radic. Biol. Med.*, 2010, DOI: 10.1016/j.freeradbiomed.2010.06.011.
5 M. Vignoni *et al.*, *Org. Biomol. Chem.*, 2010, **8**, 800.

C7

STRUCTURE AND DYNAMICS OF SUPRAMOLECULAR SYSTEMS ONE MOLECULE AT A TIME

Pierre Karam, An Ngo, Gonzalo Cosa

Department of Chemistry, Faculty of Science, McGill University, 801 Sherbrooke St.
West, Montreal, QC, H3A 2K6, Canada, email: gonzalo.cosa@mcgill.ca

Key Words: fluorescence, single molecule spectroscopy, nanomaterials

Advances in electronics, optics and nanotechnology have led to a tremendous progress in optical imaging over the past years. In the specific case of fluorescence imaging, the possibility of visualizing *single* fluorescent molecules with exquisite spatial and temporal resolution gave rise to the field of Single Molecule Spectroscopy (SMS). This technique has provided new paradigms in chemical biology, biochemistry and biophysics by revealing unique information otherwise hidden in ensemble measurements.

A major interest in our research activities is to expand SMS methods to study and characterize nanomaterials and supramolecular systems. In this presentation I will describe our recent progress on the single particle imaging of DNA nanotubes of various architectures.[1] I will also discuss our single molecule spectroscopy characterization of liposome beacons, liposomes encapsulating water soluble conjugated polyelectrolytes, with an emphasis on their role in biosensing platforms.[2] In closing, I will also address our single molecule mechanistic enzymatic studies, where we are investigating the molecular structure and dynamics of key protein/nucleic acid complexes that are intermediates in polymerase catalyzed RNA synthesis.[3]

[1] Lo, P. K. *et al.* *Nature Chem.*, **2010**, 2, 319-328.. Aldaye, F. A. *et al. Nature Nanotech.* **2009**, 4, 349-352.

[2] Ngo, A. T. *et al.* *J. Am. Chem. Soc.*, **2008,** 130, 457-459. Ngo, A. T. *et al.* *Langmuir*, **2010**, 26, 6746-6754. Karam *et al. Proc. Nat. Acad. Sci. USA.* **In press**, 2010-08068.

[3] Karam *et al.* in preparation.

C8

THE ROLE OF WATER STRUCTURE IN THE PHOTOINDUCED ISOMERIZATIONS IN CHROMOPROTEINS, IN TRIPLET STATE FORMATION, AND IN PHOTOINDUCED ELECTRON TRANSFER REACTIONS

Silvia E. Braslavsky
Max-Planck Institute for Bioinorganic Chemistry, Mülheim an der Ruhr, Germany
braslavskys@mpi-muelheim.mpg.de

Keywords: laser-induced optoacoustic spectroscopy; entropic control; hydrogen bond

Studies by Jean-Louis Habib-Jiwan and Claudio Borsarelli[1] showed that intra- and intermolecular electron transfer (ET) reactions involving Ru(II)bipyridin cyano complexes in aqueous solutions are controlled by entropy changes of the medium. The hydrogen bond network, when perturbed by added ions, influences both the enthalpy and structural volume changes for the reaction, as observed by laser-induced optoacoustic spectroscopy (LIOAS). The structural volume changes are a direct measure of the entropy changes in the aq. solutions and an enthalpy-entropy compensation effect is found for the ET reaction step, indicating that the changes in the thermodynamic parameters for this step are dominated by the chromophore-water interactions. Luis Crovetto and Víctor Martínez-Junza observed that the ET reactions between triplet flavins and electron donors (amino acids and amines) are determined by the entropic changes of the water structure around the electron exchanging pair.[2] An entropy change also accompanies free-base porphyrin triplet-state formation in aq. solution. The enthalpy extrapolation at zero structural volume change (*i.e.*, at no entropy) affords a triplet energy identical to that determined at 77K, whereas the apparent enthalpy change for triplet formation is much smaller at room temperature.[3]

An enthalpy-entropy compensation effect was found by Aba Losi for the thermodynamic parameters of the decay, to the next intermediate L, of the red-shifted intermediate with isomerized chromophore (K_{510}) produced upon photoexcitation of the photophobic sensor (pSRII) of *Natronobacterium pharaonis* in a variety of aq. media (various ionic strengths, detergent, and lipids in different concentrations). The compensation is due to subtle environment changes in the equilibrium between fluctuating structures (substates) linked to the various possible chromophore conformations, most likely resulting in different number and strength of hydrogen bonds and salt bridges.[4]

Thus, entropy changes control various types of photoinduced reactions in aq. media, due to restructuring of the hydrogen bond network upon photoinduced changes in charge distribution.

1. Habib Jiwan, J.-L.; Wegewijs, B.; Indelli, M.T.; Scandola, F.; Braslavsky, S.E. *Recl. Trav. Chim. Pays-Bas*. **1995**, *114*, 542; Borsarelli, C.D.; Braslavsky, S.E. *J. Phys. Chem. B* **1997**, *101*, 6036.
2. Crovetto, L.; Braslavsky, S. E. *J. Phys. Chem. A*, **2006**, *110*, 7307.
3. Andrés, G.O.; Cabrerizo, F.M.; Martínez-Junza, V.; Braslavsky, S.E. *Photochem. Photobiol.* **2007**, *83*, 503.
4. Losi, A.; Wegener, A. A.; Engelhard, M.; Braslavsky, S. E. *J. Am. Chem. Soc.* **2001**, *123*, 1766.

ORAL PRESENTATIONS

OC1

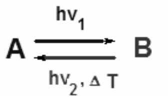
PHOTOCHROMIC ORGANIC SYSTEMS FOR PHOTOCONTROLLED RENEWABLE METAL IONS SENSING

Valery Barachevsky, Olga Kobeleva. Tatyana Valova, Alexander Gorelik

Institution of the Russian Academy of Sciences, Photochemistry Center of RAS,
Moscow, Russia, 119421, 7a-1, Novatorov Str., barva@photonics.ru

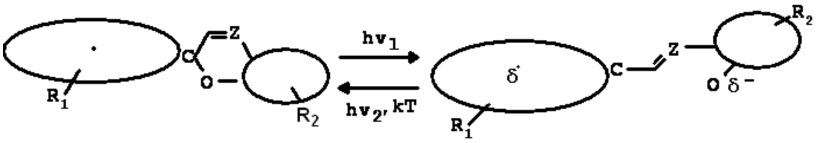
Key Words: Photochromism, complexation, metal ions

Photochromism is photoinduced reversible color change of organic and inorganic substances usually between two A and B stages:

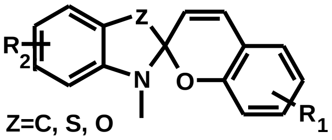


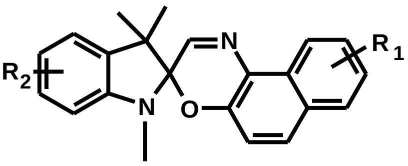
This phenomenon has a few real and potential applications. Our talk is devoted to application of photochromic organic systems based on spirocompounds for making chemosensors providing the quantity analysis of metal ions in the water systems and using for a lot of different aims: environmental monitoring, aquatic ecology, water purification, chemical and biotechnology, medicine, etc.

Molecules of spirocompounds manifest photoinduced reversible transformations between A and B states which are characterized by different reaction activity to intermolecular interaction including metal ions.

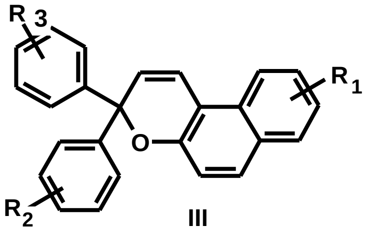


This paper presents the analysis of own results received during 10 years in the field of photoinduced complexation between molecules of spirocompounds (spiropyrans I,. spirooxazines II and chromenes III) and metal cations of the different type.





II



III

The comparative study of the photoinduced complexation between molecules of the photochromic spirocompounds and cations of the different metals showed that chelation process is not single for these compounds.

The effects of the molecular structure and metal nature as well as the interplay between a character of formed complexes and complexation centers have been established. These effects provide selective sensing for certain metal cations.

Using obtained results photochromic chemosensors have been suggested.

This work was supported by ISTC (project #3981).

OC2

EUROPIUM-BASED LUMINESCENT HYBRID FILMS FOR METAL DETECTION: A POTENTIAL COPPER (II) SENSOR

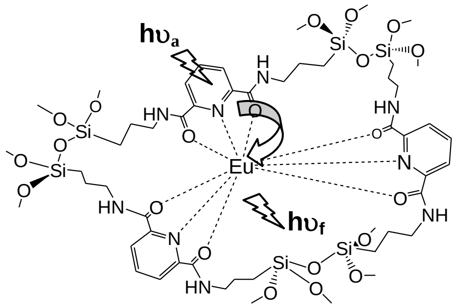
Fabricio Iglesias, Milagros Bernardi, Sara Bari and Beatriz Barja

INQUIMAE and Depto. Química Inorgánica, Analítica y Química Física.
Facultad de Ciencias Exactas y Naturales. UBA. Pabellón 2. Ciudad Universitaria.
C1428EHA Buenos Aires. Argentina

Keywords: europium, films, copper

Lanthanide ions display a well-defined luminescence characterized by narrow and highly structured emission bands with lifetimes in the millisecond timescale[1]. Strongly luminescent materials are obtained by incorporating lanthanide complexes in hybrid matrices prepared from organic silanised precursors[2].

In this work we synthesized a bridged polysilsesquioxane hybrid in which a highly luminescent Eu(III) complex of 2,6,-piridindicarboxylic acid is grafted covalently to the backbone of the silica network. Gels were synthesized with and without a templating agent (CTAB) to study the influence of the porosity of the materials. The Eu(III) luminescent hybrid sols obtained were deposited on glass slides by dip-coating, left ageing for 20 days and thermally treated at 60^{o}C. Luminescence quenching experiments with templated (TF) and non-tempated (NTF) films were performed in-situ by the addition of aqueous solutions of Fe(III), Co(II), Ni(II) and Cu(II) (λ_{exc}= 290 nm, λ_{em}= 615 nm).



Linear Stern Volmer plots were obtained for the TF being the constants K_{SV} = 2.5.10^{5} M^{-1}, 8027 M^{-1}, 6313 M^{-1} and 4075 M^{-1} for Cu(II), Ni(II), Fe(III) and Co(II), respectively. Cu(II) showed an unusual deactivation efficiency when compared with the rest of the metals, attaining detection limits of almost 50 ppm for 10 % deactivation.

Stern Volmer plots for NTF showed a downward curvature for similar Io/I ratios which could be fitted to Freundlich isotherms. NTF recovered almost 100% of their original I_o value when washed with water, independently of the metal, indicating that physisorption could be the mechanism responsible for the deactivation of the luminescence. This result is in line with a lower porosity and therefore accessibility of the metal ions to the emissive Eu(III) centers in the NTF.

(1) J. C. Bunzli and C. Piguet. *Chem. Soc. Rev.* 2005, 34, 1048-1077
(2) K. Binnemans. *Chem. Rev.,* 2009, 109, 4283–4374

OC3

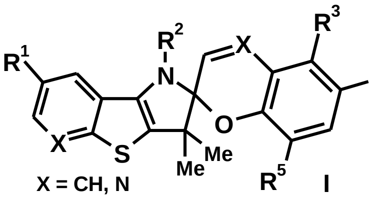
PHOTOACTIVE COMPOUNDS ON BASIS OF THIOPHENES

Mikhail Krayushkin

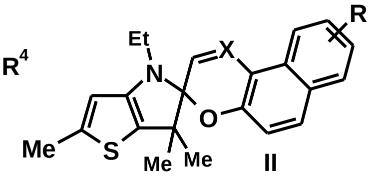
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences; 47 Leninsky prosp., 119991, Moscow, Russia. E-mail: mkray@ioc.ac.ru .

Key Words: thiophenes, photochromic spirocompounds, dihetarylethenes and fulgimides, archival and operative optical memory

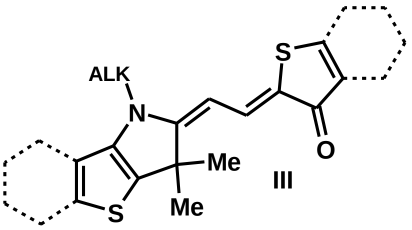
First photochromes and merocyanines of types I-III with thiophenes cycles instead of benzene rings were synthesized.



I

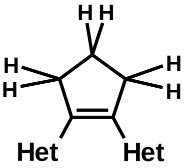


II

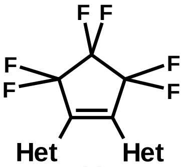


III

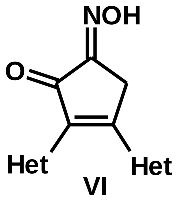
Photochromic dihetarylethenes and fulgimides IV-X possessing thermal irreversibility were prepared. Some of them can be recommended as elements for rewritable optical memory.



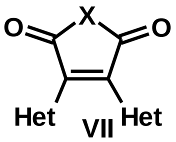
IV



V

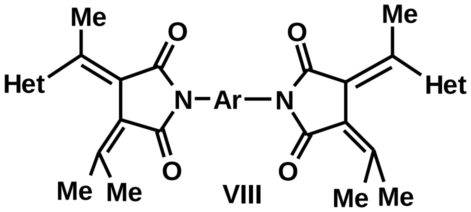


VI

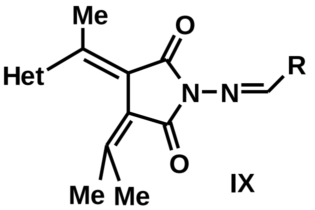


VII

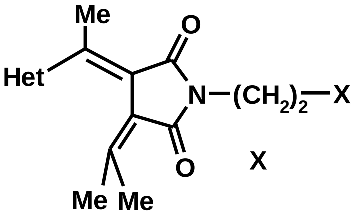
X = O, NR



VIII

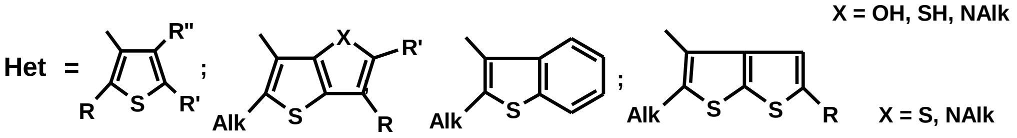


IX



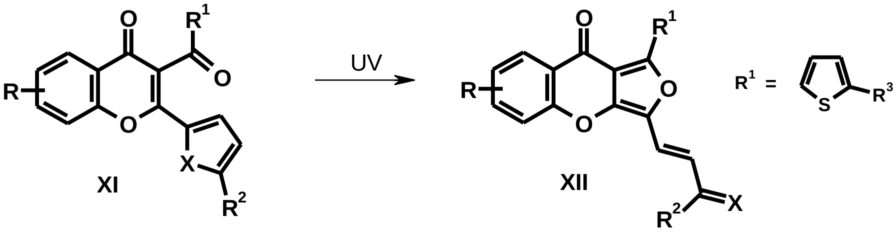
X

X = OH, SH, NAlk



R,R',R" = H,Alk,Ar,Hal,CHO,COOH,Het

Irreversible transformation of chromones XI into fluorescent compounds XII allows to apply them for archival optical memory.



OC4

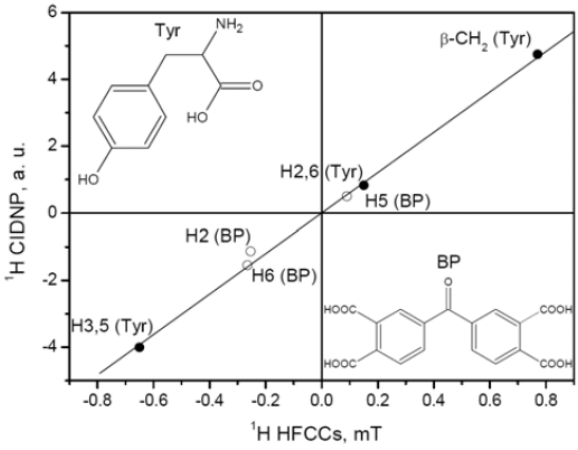
TR-CIDNP AS TOOL FOR QUANTITATIVE ANALYSIS OF HYPERFINE COUPLINGS IN ELUSIVE RADICALS

Alexey Kiryutin[1], Konstantin Ivanov[1], Olga Morozova[1], Alexandra Yurkovskaya[1], Talea Köchling[2] and Hans-Martin Vieth[2]

[1] International Tomography Center SB RAS, Novosibirsk, Russia
[2] Freie Universität Berlin, Berlin, Germany, hans-martin.vieth@physik.fu-berlin.de

Key Words: transient radicals, hyperfine couplings, CIDNP

Theoretical and experimental studies are presented showing the possibility of extracting hyperfine coupling constants (HFCCs) in radicals from their geminate CIDNP spectrum recorded at high magnetic field. First, we checked experimentally for radicals with known HFCCs that the CIDNP intensities, P_i, in the geminate spectrum are proportional to the corresponding HFCCs, a_i. As a test system we chose the photosensitizer 3,3',4,4'-tetra-carboxybenzophenone (BP), and L-tyrosine (Tyr) as an electron donor, because the HFCCs are known for both radicals from EPR experiments. The CIDNP dependence on the HFCCs which is almost perfectly described by the relation $P_i=C \cdot a_i$ is shown in the Figure. The best fit with such a function is shown by the solid line; the correlation coefficient between the data and the fit function is 0.995. Theoretical estimate predicts that the relation $P_i=Ca_i$ is accurate for systems having a large number of spins even for small values of $\Delta g\beta B$. Our results open the way to determine the HFCCs of short-lived radicals from their geminate CIDNP spectrum. Thus, time resolved (TR-) CIDNP because it selectively can measure the geminate polarization is a unique tool for analyzing the spin density distribution in elusive radicals. Inspired by such a high precision of the simple proportionality between CIDNP and HFCCs we analyzed as an example the ^{15}N CIDNP spectrum of uniformly labeled ^{15}N-adenosine-5'-monophosphate (AMP) to determine the relative ^{15}N hyperfine constants in the cation radical of AMP. In this radical there are only two protons that acquire CIDNP, while the spin density is mainly distributed among the nitrogen nuclei. Therefore it becomes necessary to measure the HFCCs of the nitrogens. Our results show that only three nitrogen nuclei have considerable spin density, namely, N1, N3 and N10. The highest spin density is localized on the amino group (N10). As a result, we obtain the following relation for the ^{15}N HFCCs: $a_{N1}:a_{N3}:a_{N10}=0.25:1:2.07$. To our knowledge it is the first time that TR-CIDNP results are obtained for ^{15}N.



Acknowledgements. This work was supported by RFBR (#09-03-00837-a, #09-03-91006-FWF_a), Presidium of SB RAS (project No. 28) and FASI (contract 02.740.11.0262)

OC5

PHOTOCHEMISTRY OF β-LAPACHONE DERIVED DIPHENYLDIHYDRODIOXIN: GENERATION AND CHARACTERIZATION OF ITS CATION RADICAL

José Carlos Netto-Ferreira[1,2], Virginie Lhiaubet-Vallet[2], Bauer Bernardes[1], Aurelio Baird Buarque Ferreira[1] and Miguel Ángel Miranda[2]

[1] Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Brazil.
[2] Instituto de Tecnología Química, Universidad Politécnica de Valencia, Spain.
jcnetto@ufrrj.br

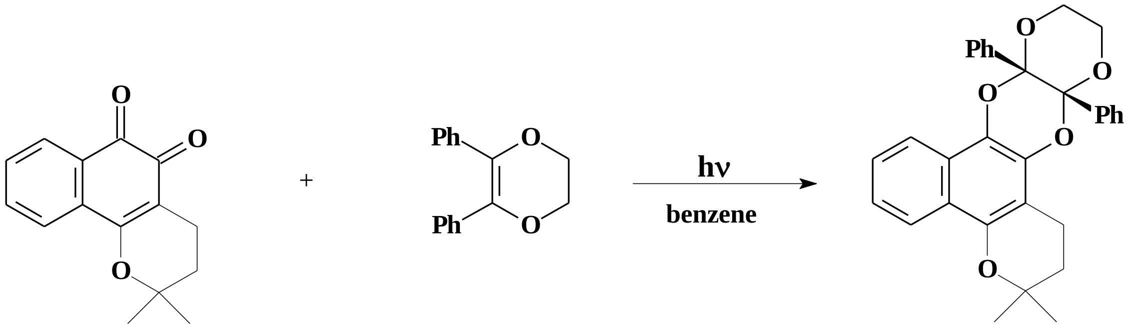
Keywords: β-lapachone; dioxin; cation radical; laser flash photolysis

The photochemical reaction of β-lapachone (**1**) and 2,3-diphenyl-*para*-dioxene results in the formation of the corresponding [4+2] cycloaddition product **2** in very good chemical yield (Scheme 1). Molecular mechanics calculations suggest that the ring formed has *cis* configuration.

Direct laser excitation (355 nm) of **2**, in acetonitrile, leads to the formation of a readily detectable transient (λ_{max}=410 nm and a shoulder at 460 nm; τ=3.5 μs) that was not quenched by oxygen or triplet quenchers. This transient was assigned to the cation radical derived from **2**. On the other hand, sensitized laser irradiation of **2**, employing benzophenone as sensitizer, resulted in the formation of its triplet state (λ_{max}=460 nm) which ultimately decays to the cation radical.

The cation radical derived from **2** can also be formed thermally through its treatment with (4-bromophenyl)aminium hexachloroantimonate (BAHA), in dichloromethane. In this case the cation radical is fairly stable, decaying in hundreds of minutes. Product analysis revealed that decay of this cation radical, generated either photochemically or thermally, results in the release of β-lapachone (**1**).

These results indicate that the photochemical release of β–lapachone from its diphenyldihydrodioxin adduct might constitute a useful tool for masking this highly reactive *ortho*-quinone.



(1) **(2)**

OC6

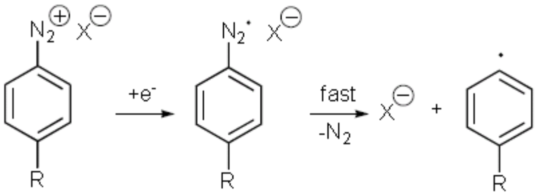
ON-OFF QD SWITCH THAT MEMORIZES PAST RECOVERY FROM QUENCHING BY DIAZONIUM SALTS

María González-Béjar[*], **Marta Liras and Juan C. Scaiano**

[*] Department of Chemistry and C*entre for Catalysis Research and* Innovation, University of Ottawa, Ottawa, Ontario, K1N 5N6.; E-mail: maria@photo.chem.uottawa.ca

Palabras clave: Quantum dots, fluorescente, electron transfer.

Diazonium salts readily lose N_2 by either direct photoexcitation or through electron transfer processes.[1] Direct photoexcitation yields highly reactive aryl carbocations, while the (frequently favored) electron transfer process tends to yield aryl radicals also highly reactive towards a wide range of substrates, both organic and inorganic (scheme 1).



Scheme 1. Electron transfer processes of diazonium salts.

We wondered what effect diazonium salts could have on the spectroscopy of semiconductor nanocrystals, and whether photoinduced electron transfer could be used to modify these particles. With these ideas in mind, we explored the interaction of core-shell CdSe/ZnS quantum dots (QD) with a simple diazonium salt ($R=CH_3$ in scheme 1). The surface of CdSe/ZnS quantum dots (QD) can be modified by diazonium salts (although not functionalized) showing and on-off fluorescence behavior that memorizes past quenching recoveries.

Overall our results lead us to conclude that diazonium salt provides an easy route for the modification and protection against quenching of core-shell CdSe/ZnS QD. However, due to the catalytic activity of the Aryl-Zn species this method does not lead to organic surface modification under our conditions. Beyond this conclusion, we have learned that diazonium salt offer a simple experimental “trick” to apply DLS measurement where under normal conditions these measurement are sometimes prevented by fluorescence interference. Further, diazonium quenching occurs by combination of static and dynamic processes that can be fitted with a Perrin model in a similar manner as non binding nitroxides. Upon photoexcitation an electron transfer proccess from the QD to the diazonium salt leads to the generation of Aryl-Zn species which in presence of BF_3 gives rise to *p*-difluoroboranetoluene. Once all the quencheable sites on the QD surface have been used, diazonium salt cannot quench the QD anymore and this new protected surface has different (attenuated) reactivity towards other quenchers, such as **4-aT**.

1 J. C. Scaiano and N. Kin-Guyen, *Can. J. Chem.*, 1982, **60**, 2286-2291.

OC7

FOTODEGRADACIÓN DE ANTIBIÓTICOS βETA LACTAMICOS

Eugenia Reynoso[1], Andrea Nesci[2], Susana Criado[1], M. Alicia Biasutti[1]

[1] Departamento de Química, Facultad de Ciencias Exactas, [2] Departamento de Microbiologia, Fco. Qcas. y Naturales, Universidad Nacional de Río Cuarto, Río Cuarto, Argentina, Dirección, e-mail:ereynoso@exa.unrc.edu.ar

Palabras clave: Fotodegradación, Antibióticos, Oxigeno Singlete

Es de suma importancia contar con estudios que provean una evaluación crítica sobre los procesos fotoquímicos globales, y en especial sobre la fototoxicidad o variaciones en las propiedades específicas de drogas, medicamentos, cosméticos, y suplementos /aditivos alimenticios consumidos por el ser humano. Aunque muchos de estos compuestos son almacenados sin prevención ante la luz natural medioambiental, dado que son transparentes a la misma, pueden existir en el medio compuestos coloreados, capaces de absorber la radiación natural y producir, a través de diferentes mecanismos, daños degradativos sobre aquellos sustratos transparentes. Los antibióticos y bacteriostáticos, transparentes a la fotoirradiación directa con luz natural, pertenecen a esta clase de sustratos biológicamente activos y comercialmente importantes. La principal motivación de los estudios con agentes implicados en tratamientos de la salud humana, radica en la evaluación de la extensión y naturaleza del daño fotooxidativo producido como resultado de las interacciones con las especies reactivas de oxigeno y sus implicancias microbiológicas. En este contexto, se abordo el estudio de antibióticos beta-lactamicos: Amoxicilina:(Am), Cefalexina (Cf) y Ceftriaxona (Cft). Se investigó (a) la fotoxidación de Am, Cf y Cft mediada por oxígeno singlete molecular ($O_2(^1\Delta_g)$), especie generada utilizando Rosa de Bengala (RB) como fotosensibilizador y (b) las implicancias microbiológicas que dicho proceso puede producir sobre los sustratos y su actividad terapeutica. La cinética de fotooxidación de los antibióticos, se siguió a través del consumo de sustrato por espectroscopía de absorción y de consumo de oxígeno, en condiciones aeróbicas de fotoirradiación estacionaria, para determinar las constantes de velocidad para el "*quenching*" de $O_2(^1\Delta_g)$ químico (k_r), a pHs 6, 7.4 y 12. Las constantes de velocidad para el "*quenching*" total (k_t) de $O_2(^1\Delta_g)$, se determinaron por medidas de fosforescencia IR resuelta en el tiempo (TRPD). Para Am y Cf los valores de k_r y k_t son mayores a pH básico que neutro, siendo para Am dos ordenes de magnitud mayor, indicando que el proceso fotooxidativo, mediado por $O_2(^1\Delta_g)$ es favorecido a pH básico por la ionización de su grupo fenólico. Para Cft no se observaron cambios tan significativos con la variación de pH.

Por otro lado, se realizaron ensayos microbiológicos con cepas de *Staphylococcus aureus* al pH fisiológico, con el fin de determinar la influencia de la fotooxidación sobre las propiedades bactericidas de los antibióticos. Los resultados microbiológicos muestran claramente que la fotodegradación es acompañada por una perdida neta de actividad bactericida.

OC8

SITE-SELECTIVITY IN ELECTRON TRANSFER PHOTOREACTION OF DIPEPTIDE.

Alexandra V. Yurkovskaya[*,1], **Natalia S. Saprygina**[1], **Olga B. Morozova**[1], **Hans-Martin Vieth**[#]

[*,1]International Tomography Center SB RAS Institutskaya 3A, Novosibirsk 630090
Russian Federation, yurk@tomo.nsc.ru

Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany, vieth@physik.fu-berlin.de

Key Words: photo-CIDNP kinetics, tryptophan-tryptophan, electron exchange

Chemically Induced Dynamic Nuclear Polarization (CIDNP) kinetics of laser induced photo-oxidation of tyrpophan-tryptophan (HTrp-TrpOH) dipeptide has been studied in aqueous solution at variable pH. The time-resolved version of the CIDNP technique utilizes the structural information available from NMR spectroscopy for monitoring the chemical and structural changes associated with particular atoms during fast radical reactions on a microsecond time-scale. It was found that the quenching of photoexcited 2,2'-dipyridyl triplets by HTrp-TrpOH depends on the pH of aqueous solutions. In acidic and neutral solutions the terminal amino group is protonated and the quenching by electron transfer proceeds very selectively: only the residue at the C-terminal of dipeptide is involved. Intramolecular electron transfer does not occur at these conditions and only the C-terminus of the peptide is polarized during the time domain. Generated radical, like free amino acid radical, participates effectively in the degenerate reaction of electron exchange with a diamagnetic peptide molecule. This degenerate reaction proceeds very selectively with the formation of the radical center only on the C-terminal tryptophan residue of the peptide. At pH above the p*K*a of terminal amino group both residues of the peptide involved in the quenching of the dipyridyl triplets. Two types of cation-radicals of the peptide formed: with radical centers at C- or N - terminal tryptophan residues of the peptide. Due to fast deprotonation of tryptophanyl cationradicals at both termini the degenerate electron transfer also does not occur under these conditions.

The financial support of RFBR (projects No. 08-03-00539-a, 09-03-00837-a, 09-0391006-FWF_a), Program of RAS (project 5.1.1), SB RAS (project No. 28), State contract 02.740.11.0262 is acknowledged.

OC9

SINGLE MOLECULE TECHNIQUES TO STUDY CHARGE TRANSFER AT ELECTRODE INTERFACES

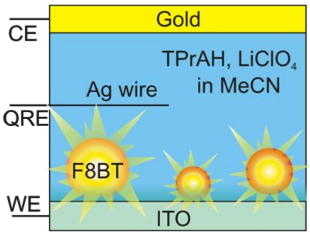
Rodrigo Palacios

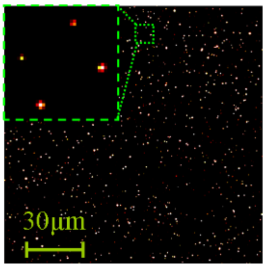
Departamento de Química, Facultad de Ciencias Exactas Físico Químicas y Naturales,
Universidad Nacional de Río Cuarto, Córdoba, Argentina, Ruta Nac. 36 - Km. 601 CP: 5800,
rpalacios@exa.unrc.edu.ar

Keywords: Single Molecule Spectroscopy, Charge Transfer, Conjugated Polymers

I will discuss new approaches to study electron transfer processes at highly heterogeneous interfaces using the recently developed technique, Single Molecule Spectroelectrochemistry (SMS-EC). The technique uses florescence spectroscopy to measure the electrochemical behavior of single molecules and nanoparticles (NPs), one at a time. This unique ability was used to uncover, for the first time, the distribution of single molecule oxidation potentials in conjugated polymers, a novel class of organic electronic materials used in promising strategies for solar cells, flat-panel displays, and chemical sensors. Several conjugated polymers -including F8BT, MEH-PPV, and BEH-PPV- were studied at the single molecule and NP level. In the case of single molecules, the results reveal both excited singlet state and ground state oxidation. In the case of NPs two main processes have been observed: an irreversible chemical reaction (occurring when the particle is highly oxidized) and a reversible hole-injection charging process. The latter seems to occur primarily by initial injection of shallow (untrapped) holes (positive charge carriers), but soon after the injection a small fraction of the holes becomes deeply trapped.

In a different application SMS-EC was used to demonstrate, for the first time, the Electrogenerated Chemiluminescence (ECL) of single conjugated polymer NPs. In this case SMS-EC allowed the study of the dynamics of the ECL process. Thus, in addition to the usual advantage of single particle studies of obtaining information about particle environments, this approach may also provide dynamic information not seen in ensembles. Moreover, because of high sensitivity, low background, and relatively high spatial and temporal resolution of ECL, this new method could be useful as a sensitive analytical technique. Lastly, a variation of SMS-EC and ECL was used to study the spatial evolution of electrochemical oxidation in thin conjugated polymer films.





References

"Electrogenerated Chemiluminescence of Single Conjugated Polymer Nanoparticles." Chang Y-L. , **Palacios R.E.**, Fan F-R.F., Bard A.J., Barbara P.F. *JACS*, **2008**,130(28), 8906

"Charging and Discharging of Single Conjugated-Polymer Nanoparticles." **Palacios R.E.**, Fan F-R.F., Bard A.J., Barbara P.F. *Nature Materials*, **2007,** 6, 680-685.

"Single Molecule Spectroelectrochemistry (SMS-EC)." **Palacios R.E.**, Fan F-R.F., Bard A.J., Barbara P.F. *JACS Communication.* **2006**, 128(28), 9028-9029.

OC10

EFFECT OF ZINC CHELATION ON PDT ACTIVITY OF PORPHYRINS: SUBCELLULAR LOCALIZATION AND CELL DEATH

Christiane Pavani[*], **Yassuko Iamamoto**[#], **Maurício S. Baptista**[*]

[*]Departamento de Bioquímica, Instituto de Química, Universidade de São Paulo, Brasil,
christp@usp.br; baptista@iq.usp.br
[#]Departamento de Química, FFCLRP- USP, Ribeirão Preto, Brasil, iamamoto@usp.br

Keywords: ZincPorphyrin, Photodynamic therapy, Apoptosis

A series of photosensitizers (PS), which are meso-substituted tetra-cationic porphyrins, was synthesized and characterized in order to study the role of amphiphilicity and zinc insertion in PDT efficacy. The photophysical properties of all compounds are quite similar (absorption maxima in the same region of the spectra, $\Phi f \leq 0.02$; $\Phi\Delta \sim 0.8$). Increase in lipophilicity and the chelation of zinc in the porphyrin ring result in higher vesicle and cell uptake. Binding in mitochondria is dependent on the PS lipophilicity and on the electrochemical membrane potential. Zinc insertion was also shown to decrease the interaction with isolated mitochondria and with the mitochondria of HeLa cells, an effect that has been explained by the particular characteristics of the mitochondrial internal membrane. Phototoxicity was shown to increase proportionally with membrane binding efficiency, which is attributed to favorable membrane interactions between FSs and membranes, which allow for more efficient membrane photoxidation. Zinc chelation is related with higher membrane binding and higher photodynamic efficiency. These effects are attributed to a complexation of zinc with the phosphate groups of the phospholipids. Mechanistic studies on cell death are been developed to establish relationships between cytolocalisation and cell death by a necrotic or apoptotic mechanism. Thus, for this series of compounds, photodynamic efficiency is directly proportional to membrane binding and cell uptake, but it is not totally related to mitochondrial targeting.

OC11

EFFECT OF PHOTO-OXIDATION ON THE INTERACTION OF CYTOCHROME *C* WITH INNER MITOCHONDRIAL MIMETIC MEMBRANE

Cintia Kawai,[1] Tathyana Tumolo,[1] Iseli Nantes,[2] Mauricio S. Baptista[1]

1 Departamento de Bioquímica, Instituto de Quimica, USP, Brazil.
cintiakawai@yahoo.com, baptista@iq.usp.br
2 Universidade Federal do ABC, Santo Andre, SP, Brazil.

During photo-induced cell death the release of cytochrome *c* (cyt*c*) from mitochondria to cytosol is a key step that is responsible for the activation of the intrinsic pathway of apoptosis. Therefore, the interaction between cyt*c* and the inner mitochondrial membrane (IMM) has fundamental importance for the understanding of photo-induced cell killing. By surface plasmon resonance and fluorescence techniques we studied the adsorption of cyt*c* to vesicles and hybrid bilayer membranes, which mimic the IMM. The adsorption of native cyt*c* shows a cooperative profile, which is due to reorganization of the lipid molecules and the formation of phospholipid domains as indicated by literature data and Atomic Force Microscopy results. The cooperativity was treated quantitatively by an adaptation of Hill's model that considers the existence of two dissociation rate constants and the coefficient *m* (cooperativity constant).(1) kd1 is related with electrostatic interactions and kd2 is related with hydrophobic interactions. kd1 and *m* decrease with the increase in pHs 6.8, 7.4 and 8.0, showing that the increase in affinity is correlated with a decrease in cooperativity, which is in accordance with the deprotonation of cardiolipin lipids in the interface. The dissociation of native cyt*c* requires a minimum concentration of 30 mM of calcium to become significant. Photo-oxidized cyt*c* (*cyt405*)(2) showed lower kd1 and m values when interacting with the same IMM. Moreover, our results indicate that *cyt405* is not easily dissociated by calcium due to loss of cooperativity in the interaction. These results, as well as literature data(3), indicates that *cyt405* is not responsible for the initiation of apoptosis. Another possible explanation for the release of cyt*c* would be lipid oxidation. We investigated the interaction of cyt*c* with IMM mimetic liposomes containing either oxidized phosphatidylcholine PazePC (1-O-Hexadecyl-2-Azelaoyl-sn-Glycero-3-Phosphocholine) or lipid hydroperoxide prepared from POPC (POPCox), at pH 7.4 and 6.2. The presence of PazePC (1-O-Hexadecyl-2-Azelaoyl-sn-Glycero-3-Phosphocholine) increased K_D^1 value one thousand fold at pH 6.2. We characterized a strong interaction of PazePC with cyt*c*, at this pH. The presence of POPCox also diminished the K_D^1 value but caused a significant increased on K_D^2 value in both pHs. The expressive in K_D^2 in the presence of POPCox can be related to the detachment process of cyt*c* from IMM and consequently to trigger the apoptotic process. 1. Suraniti, E. et al *Langmuir* 2007**,** *23,* 6835. 2. Estevam, M.L. et al *J.Biol.Chem.* 2004, 279, 39214. 3. Rodrigues, T. et al *J. Biol. Chem.* 2007, 282, 25577.

Supported by FAPESP and CNPq

OC12

WAVELENGTH – SELECTIVE FLUORESCENCE TECHNIQUES TO CHARACTERIZE ORGANIZED SYSTEMS

R. Dario Falcone, Fernando Moyano, Silvina Quintana, Juana J. Silber, N. Mariano Correa

Departamento de Química. Universidad Nacional de Río Cuarto.(CP X5804ZAB) e-mail
rfalcone@exa.unrc.edu.ar

Palabras clave: Reverse Micelles, Vesicles, REES

Reverse micelles (RMs) are surfactant aggregates formed in non-polar solvents with their polar groups concentrated in the interior. They have been evaluated as a unique and versatile medium for a variety of chemical reactions, such as nanoparticles preparation and organic or bioorganic synthesis. Among the surfactants capable of forming reverse micelles, the most widely used is the anionic surfactant sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT). Other interesting organized media are the liposomes or vesicles. Vesicles are spherical self-closed structures, formed by some amphiphilic compounds. The lipid bilayer surrounds an aqueous void volume which can be "loaded" with almost any variety of water-soluble marker molecules. Therefore, the vesicles may contain both lipophilic and water-soluble substances.

Fluorophores may show excitation wavelength dependence if the dipolar relaxation of the solvent molecules is slow in the excited state, such that the relaxation time is comparable to or longer than the fluorescence lifetime. Such a shift in the wavelength of maximum emission toward higher wavelengths, caused by a shift in the excitation wavelength toward the red edge of the absorption band, is known as the red edge excitation shift (REES). Wavelength – selective fluorescence comprises a set of approaches based on the red edge effect in fluorescence spectroscopy. This approach can be used to directly monitor the microenvironment and dynamics around a fluorophore in a motion restricted media such as organized media like RMs or vesicles.

In this work we report the behavior of two different hemicyanines: trans-4-[4-(dimethylamino)-styryl]-N-methylpyridinium iodide (HC) and, 4-[4-(dihexadecylamino)-styryl]-N-methyl-pyridinium iodide (DIA) in water/AOT/benzene RMs media and in large unilamellar vesicles (LUV) of the phospholipid 1,2-di-oleoyl-*sn*-glycero-3-phosphatidylcholine (DOPC), using absorption, emission, depolarization and time-resolved spectroscopies. The results in the present work introduce HC and DIA as very good probes to study the dynamics of confined environments trough the wavelength–selective fluorescence approach. In AOT RMs, we present a nice, simple and noteworthy method that help to examine the presence or the absence of organized media. In DOPC LUV media, the results show that the fluid state of the bilayer resembles the microenvironment of AOT RMs at W = $[H_2O]/[AOT]$ below 10 and it is demonstrated for the first time, that the region of the bilayer close to the polar head of DOPC is a powerful electron donor environment.

OC13

EVALUACIÓN DE LA ASOCIACIÓN SOLUTO/PROTEÍNA MEDIANTE MEDIDAS DE FLUORESCENCIA

Eduardo Lissi,* **Emilio Alarcón*, Ana María Edwards$^{\#}$, Elsa Abuin* y Alexis Aspée***

(*) Universidad de Santiago de Chile, Facultad de Química y Biología, Av. Bernardo O'Higgins 3363, Santiago, Chile. E-mail: eduardo.lissi@usach.cl
(#) Pontificia Universidad Católica de Chile, Facultad de Química

***Palabras clave*: asociación soluto/proteína; Rosa de Bengala; Azul de metileno; Merocianina 540**

La asociación de solutos a proteínas es un tema de interés, tanto desde el punto de vista de la fisicoquímica básica como por sus aplicaciones en numerosos campos de la biología. La fluorescencia estacionaria es una de las técnicas más sencilla y versátil para realizar este tipo de evaluaciones, habiéndose desarrollado metodologías basadas en:

i) desplazamiento de sondas fluorescentes asociadas a la proteína;
ii) cambios en la fluorescencia del soluto cuando se asocia a la proteína;
iii) cambios en la fluorescencia intrínseca de la proteína en presencia del soluto.

Estas metodologías son frecuentemente aplicadas indistintamente y los resultados considerados como comparables. Sin embargo, la información que ellas entregan puede ser completamente distinta, dependiendo del modelo de asociación que predomine. En la presente comunicación se discutirán las ventajas y limitaciones de los distintos enfoques y cómo su uso y el significado de las mediciones depende del tipo de asociación que predomine en las condiciones experimentales del ensayo. En particular, se discutirán los resultados obtenidos en la evaluación de la asociación de colorantes (Rosa de Bengala, Azul de Metileno y Merocianina 540) a albúmina de suero humano. Los resultados serán contrastados con aquellos obtenidos mediante otras metodologías (separación de fases y cambios de absorbancia).

Agradecimientos Los autores agradecen a Fondecyt (Proyectos Nos. 1070285 y 96035), Dicyt (USACH), VRAID (PUC).

OC14

HOW THE PHOTOPHYSICS OF PRODAN AND HC CAN BE CONTROLLED USING “SMART” ORGANIZED SYSTEMS

N. Mariano Correa, Fernando Moyano, Silvina Quintana, Mercedes Novaira, R. Darío Falcone, Juana J. Silber.

Departamento de Química. Universidad Nacional de Río Cuarto.(CP X5804ZAB) e-mail mcorrea@exa.unrc.edu.ar

Keywords: Dual Emission, Reverse Micelles, ICT

Reverse micelles (RMs) are aggregates of surfactant molecules with their polar groups concentrated in the interior. They have been evaluated as a unique and versatile medium for a variety of chemical reactions, such as nanoparticles preparation and organic or bioorganic synthesis. Among the surfactants capable of forming reverse micelles, the most widely used are the anionic surfactant sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) and the cationic benzyl-n-hexadecyldimethylammonium chloride (BHDC). Besides water, some polar organic solvents, having high dielectric constants and very low solubility in hydrocarbon solvents, can also be encapsulated in RMs. The most common polar solvents used include formamide (FA), dimethylformamide (DMF), dimethylacetamide (DMA), ethylene glycol (EG), propylene glycol (PG), and glycerol (GY).

The photoinduced intramolecular charge transfer (ICT) of various organic molecules containing electron donor (generally a dialkylamino group) and acceptor groups in its moiety, has been the growing interest of recent investigations since it is a possible mechanism for biological and chemical energy conversion. The ICT state is formed from the initially excited planar state. The formation of the ICT state could give a dual fluorescence phenomenon where two emission bands will be observed: the normal emission from the local excited state (LE) and a new low energy band which correspond to the ICT state.

In this work we report the behavior of two different fluorophores: trans-4-[4-(dimethylamino)-styryl]-N-methylpyridinium iodide (HC) and, 6-propionyl-2-(N,N-dimethyl) aminonaphthalene (PRODAN) in water/AOT or BHDC/benzene and EG, GY, PG, FA, DMF and DMA/AOT/n-heptane RMs, using absorption, steady-state, time-resolved fluorescence (*TRES*) and time–resolved area normalized emission (*TRANES*) spectroscopies. We show that it is possible to control the PRODAN states emission: LE, ICT or both, simply changing the properties of the AOT RMs interfaces by choosing the appropriate polar solvent to make the reverse micelles media. For HC, our results show that the hemicyanine spectroscopic behavior is completely different when dissolved in AOT or in BHDC RMs media. While the dye undergoes an ICT process upon excitation in the former media, in BHDC this process is inhibited due to the cationic nature of the surfactant, emitting for the first time, from an LE state.

Our results show that RMs interfaces can be a unique media to control some charge transfer processes of molecules that have a complicated photophysics.

OC15

PHOTOINITIATION ACTIVITY OF DYE COMPOUNDS. CORRELATION POLYMERIZATION EFFICIENCY AND PHOTOCHEMICAL BEHAVIOUR

M. V. Encinas[*], **A. M. Rufs**[*], **A. Valdebenito**[*], **S. Bertolotti**[#], **C. Previtali**[#]
[*]Universidad de Santiago de Chile, Facultad de Química y Biología, Chile. [#]Universidad Nacional de Río Cuarto, Fac. Ciencias Exactas, Físico Químicas y Naturales, Argentina.

Key words: Photopolymerizations, photoinitiators, dye compounds.

In the last years, polymerizations of vinyl monomers induced by the radiation have gained increasing relevance. This is principally due to its widespread applications, in many cases, complex polymers with well defined architecture are required. Then, the search of new photoinitiators and coinitiators is an exiting area in photopolymerizations research.

Typical photoinitiators are those that produce the active radicals by the interaction of initiator excited states with an appropriated coinitiator, frequently tertiary amines, through an electron transfer process. This indicates that the active radical yield must be highly dependent on the structural characteristics of photoinitiator and coinitiator. Strong dependence on the solvent and monomer properties and on formulation additives also is expected. In spite of this, there are not systematic studies that explain all variables involved in the active radical production. In this work we describe systematic studies on the relation of free radical photopolymerization efficiency with the photochemical behavior of structurally related photoinitiators absorbing visible radiation.

The efficiency of several xanthene dyes as photoinitiators of free radical polymerization was evaluated. The detailed study of dye photophysics under the polymerization conditions showed that the active radicals are formed in the interaction of dye excited triplet state with the amine. The experimentally measured active radical formation is well correlated with that calculated from polymerization rate. The presence of heavy atoms in the xanthene ring increases the triplet quantum yield, but decrease the active radical yield, and then the polymerization rate.

Related to the synthesis of polymers with complex architecture, we used PAMAM dendrimers of low generation as macrocoinitiators. The polymer characterization employing different techniques showed that branched polymers were successfully obtained. However, the polymerization rates and radical yields are not well correlation suggesting that the coinitiator microenvironment location is an important factor to consider.

Studies on the use of phenols as chain transfer agents of photopolymerizations showed that the efficient is strongly related to the phenol electron-donor acceptor capability. The ground state complex formation and quenching of photoinitiator excited states are the main processes that control the chain transfer efficiency.

Acknowledgment. Financial support from FONDECYT grant 1070123.

OC17

STEREOSELECTIVE INTERACTION OF EPIMERIC NEW NAPROXEN-RGD PEPTIDES WITH HUMAN SERUM ALBUMIN

María González-Béjar,[a*] Emilio Alarcón,[a] Horacio Poblete,[b] Juan C. Scaiano,[a] and Julia Pérez-Prieto.[c]

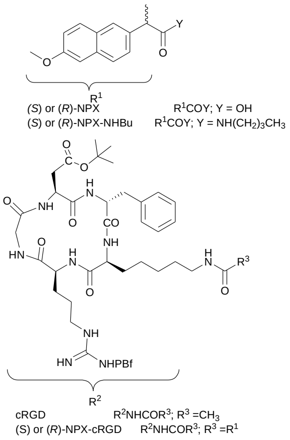
[a]Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario, K1N 6N5.

[b]Center for Bioinformatics and Molecular Simulations, Universidad de Talca, 2 Norte 685, Casilla 721, Talca, Chile.

[c]Instituto de Ciencia Molecular / ICMOL, Universidad de Valencia, C/ José Beltrán 2, 46980 Paterna, Valencia, Spain.

Key Words: RGD, naproxen, HSA, stereoselective binding, docking simulation.

The association and photophysical behavior of two new epimeric bioconjugates, which contain (*S*)- or (*R*)-naproxen (NPX) bound to a cyclopentapeptide with an arginine-glycine-aspartate sequence (cRGD), to Human Serum Albumin (HSA) was studied. Direct physical separation of the unbound compound and fluorescence quenching of the protein were employed to estimate the association constants. On the other hand, circular dichroism was used to determine the modification of the protein structure by the compound association. Finally, nanosecond laser flash photolysis experiments were carried out in order to evaluate the compound photobehavior inside the protein. Interestingly, fluorescence quenching of Trp-214 in HSA by the naproxen compounds (NPXs) revealed low efficiency for (*S*)-NPX-RGD as Trp quencher as compared to *(R*)-NPX-cRGD. Thus, although both bioconjugates bound preferentially to site I, in a different way (*S*)- and (*R*)- NPX are bound mainly to site II, only the NPX moiety of *(R*)-NPX-cRGD was located within site I pocket, as docking simulation confirmed, explaining its high efficiency for Trp-214 fluorescence quenching. These results are an excellent example about the importance of specific chiral differentiation toward HSA association.



Scheme 1. Chemical structure of the compounds under study.

Acknowledgments: NSERC, MEC (CTQ2008-06777-CO2-01, M.G.B. post-doctoral contracts), Proyecto Anillo Cientifico ACT/24, Becas Chile (E. A. post-doctoral contract), GVA (ACOMP/2009/334), UVEG (UV-AE-09-5805) and Talca University

OC18
FOTOFÍSICA DE LA FTALOCIANINA DE ZINC HEXADECAFLUORADA

Angélica García[*1], Emilio Alarcón[2], Claudia Bueno[1], Marcelo Muñoz[1] y Ana María Edwards[1].

* 1. Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile, Avenida Vicuña Mackenna 4860, casilla 306 correo 22, amgarci4@uc.cl, aedwards@puc.cl, cbuenor@puc.cl, mamunoz1@uc.cl.
2. Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Canada, K1N 6N5, emilio@photo.chem.uottawa.ca.

Palabras clave: fotofísica, ftalocianina, terapia fotodinámica.

Las ftalocianinas se caracterizan por ser compuestos macrociclicos pertenecientes al grupo de fotosensibilizadores de segunda generación potencialmente aplicables en el tratamiento fototerapéutico contra el cáncer, comúnmente denominado terapia fotodinámica. Dichos compuestos presentan excelentes propiedades tales como fotoestabilidad, altos rendimientos cuánticos de oxígeno singulete, largos tiempos de vida del estado triplete excitado, una intensa absorción a largas longitudes de onda (región roja del espectro visible). Sin embargo, su principal desventaja es su alta hidrofobicidad y por lo tanto, tendencia a formar especies agregadas, motivo por el cual se dificulta su estudio tanto a nivel fotoquímico como fotodinámico en sistemas biológicos.

La ftalocianina de zinc hexadecafluorada ($ZnF_{16}Pc$, Figura 1), ha sido empleada en algunos sistemas *in vivo*, pero su comportamiento fotofísico aún no ha sido estudiado en profundidad. En el presente trabajo se expone su comportamiento en diferentes solventes en un amplio rango de polaridad así como las principales propiedades fotofísicas (rendimientos cuánticos de tripletes y singuletes) y fotoquímicas (rendimientos cuánticos de oxígeno singulete y fotoconsumo) para el caso de los solventes tetrahidrofurano, cloroformo, dimetilformamida y dioxano. El rol de la polaridad y agregación sobre estas propiedades es discutido en esta contribución.

.

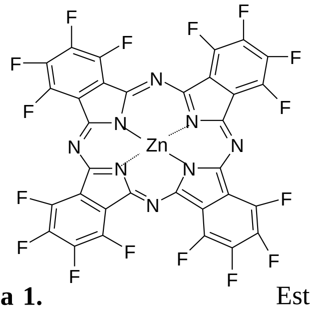


Figura 1. Estructura quimica de $ZnF_{16}Pc$

Agradecimientos
Angélica García agradece a MECESUP por su beca para estudios de doctorado así como a CONICYT por la beca de Apoyo de Tesis AT 24080085. Marcelo Muñoz agradece a CONICYT por su beca doctoral.

OC19

THE PHOTOPHYSICS OF ANTHOCYANINS

Frank Herbert Quina

Instituto de Química, Universidade de São Paulo, São Paulo, Brazil
E-mail: quina@usp.br

Anthocyanins, the major red, purple and blue pigments of plants, absorb visible as well as ultraviolet radiation and are effective antioxidants and scavengers of active oxygen species. In plant leaves, one of the functional roles proposed for anthocyanins is protection of the photosynthetic apparatus from the effects of excess incident visible or UV-B radiation and photooxidative stress. Indeed, our studies of the photochemical properties of synthetic analogues of anthocyanins and of several naturally occurring anthocyanins show that uncomplexed anthocyanins decay back to the ground state almost entirely via fast (sub-nanosecond) excited state proton transfer and that anthocyanin-copigment complexes decay entirely by fast (sub-picosecond) charge-transfer-mediated internal conversion.

Studies of ultrafast proton transfer from synthetic anthocyanins anchored at the surface of sodium dodecyl sulfate (SDS) micelles provide a detailed picture of the dynamics of proton migration on the micelle surface as moculated by water structure at the micelle surface. Finally, the fact that anthocyanins in which proton transfer is blocked by methylation or glycosylation of the 7-hydroxy group are quite rare in nature led us to perform photophysical studies of several synthetic 7-methoxy anthocyanins analogs. These compounds show evidence of the formation of triplet states (i.e., phosphorescence at 77 K) and of sensitized formation of singlet oxygen.

Supported by: CNPq and INCT-Catálise

OC20

CINÉTICA DE FOTODEGRADAÇÃO DE SOLUÇÕES DE LARANJA DE METILA UTILIZANDO NANOTUBOS DE TIO_2. EFEITO DO DIÂMETRO E COMPRIMENTO.

Camila Ribeiro*, Heberton Wender#, Adriano F. Feil#, Jairton Dupont*, Sérgio R. Teixeira# e Daniel E. Weibel*

*Instituto de Química, Universidade Federal do Rio Grande do Sul
#Instituto de Física, Universidade Federal do Rio Grande do Sul
*e-mail: danielw@iq.ufrgs.br

Palabras chave: Fotodegradação, Nanotubos, TiO_2

Processos Oxidativos Avançados têm atraído fortemente a atenção da comunidade científica nos últimos anos no tratamento de efluentes aquosos poluídos. Especialmente, se destacam os processos que utilizam semicondutores de metais de transição, onde o TiO_2 na forma nanoparticulado (pó) é, com certeza, o mais estudado. As nanoparticulas apresentam difícil remoção do meio de reação (centrifugação, ultra filtração, etc.) sendo geralmente suportadas em um sólido e perdendo, conseqüentemente, área superficial ativa. Pelo contrário, estruturas nanotubulares são auto-suportadas com grande área superficial ativa. Neste trabalho, diferentes nanotubos (NTs) de TiO_2 são utilizados na degradação fotocatalítica ultravioleta (UV) de uma molécula protótipo: laranja de metila (LM).
Os NTs de TiO_2 foram sintetizados pelo processo de anodização eletroquímica a partir de substratos de Ti (98,5%). A síntese dos NTs foi realizada em soluções de Etilenoglicol com 10 % P/P de H_2O contendo 0,6 % V/V de $BMI.BF_4$ (1-butil-3-methyl-imidazolium tetrafluorborate), NH_4F ou HF. Os NTs de TiO_2 foram caracterizados por difração de Raios-X, SEM e XPS. As reações fotocatalíticas foram realizadas num reator fotoquímico feito totalmente de quartzo de ~ 35 mL com um suporte de teflon para os NTs e com agitação permanente. Como fonte de irradiação UV se utilizou principalmente uma lâmpada Hg/Xe de alta pressão (150 W). A cinética de degradação de soluções de LM de diferentes concentrações (10-50 ppm) foi medida por espectrofotometria UV-visível com NTs de diversos diâmetros externos (D) e comprimentos (L). Três tipos de NTs foram utilizados (dimensões em μm). NT1: $BMI.BF_4$ (D = 0,4; L = 0,18), NT2: HF (D = 0,109; L = 2,08) e NT3: NH_4F (D = 0,2; L = 3,41).
Quando soluções de LM foram irradiadas na ausência ou presença de NTs de TiO_2, o resultado típico foi a fotodegradação do LM quando o fotocatalisador estava presente no meio de reação. As fotodegradações de LM em presença do NTs seguiram cinéticas de pseudo primeira ordem que podiam ser ajustadas à seguinte equação exponencial:

$$C_t = C_0 \exp(-k_a t)$$

Para o NT3, o mais ativo fotocatalisador utilizado, a constante aparente de reação medida foi de 0,0016 min^{-1} quando a concentração de LM utilizada foi de 10 ppm. Nessa concentração, k_a mostrou a seguinte seqüência na fotodegradação de LM: NT1 $\leq$ NT2 < NT3, provavelmente indicando um aumento relativo na área superficial dos NTs. Novas experiências estão sendo desenvolvidas normalizando as dimensões dos NTs sintetizados.

OC21

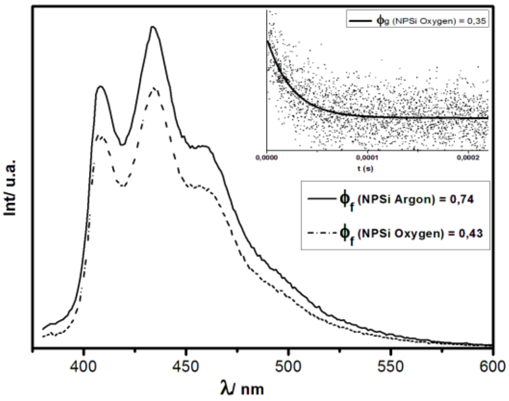
SILICON NANOPARTICLES: SINGLET OXYGEN GENERATION

Manuel J. Llansola Portolés[a], Pedro David Gara[b], Mónica C. González[a], Daniel O. Martire[a],

[a] INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, (1900) La Plata. e-mail: mjllansola@gmail.com
[b] CITOMA, Fundación Avanzar, Instituto de Terapia Radiante, CIO La Plata. Avenida 60 Nro 480 (1900), La Plata.

Palabras clave: Silicon nanopaticles, single oxygen, multiphotonic

Diameter size silicon nanoparticles (SiNP) of a few nanometers show strong photoluminescence due to quantum confinement with maximum wavelength emission strongly depending on size, superficial coating and environment. In addition, Si-NPs are photosensitizers of reactive oxygen species. These properties make them excellent candidates for diagnosis proposes (specific luminescent markers) and for therapeutic treatments. In the aim of evaluating the potential application of derivatized SiNP in biological systems, we undertook the synthesis of SiNP of (3 ± 1) nm sizes functionalized with organic groups like methylmethacrylate and vitamin B9. The electrochemical synthesis and subsequent surface derivatization of 3 nm diameter yield silicon nanoparticles of surface composition $Si_3O_6(C_5O_2H_2)$ and strong blue photoluminescence. The short lifetime of 1 ns observed for the decay of the luminescence supports a direct band gap transition which could result from the rapid trapping of the exciton at the nanocrystal surface. The participation of surface irregularities in the emission originated from the recombination of holes and trapped electrons was supported by the value of anisotropy at time zero and the large Stokes shift. Excitation-emission spectra and quantum yields were obtained in monophotonic excitation experiments. The figure shows the emission spectrum of SiNP in toluene suspensions. Dissolved oxygen reduces the emission quantum yield (Φ_f) around a 31 % the value in oxygen free suspensions. Multiphotonic excitation at 774 nm leads to the same emission spectra than monophotonic experiments, as well as similar oxygen effects.



Although observation of the luminescence quenching by molecular oxygen may be an indication of energy transfer from excitons to oxygen molecules, it is still not an evidence for singlet oxygen ($^1O_2$) generation. Therefore, detection of $^1O_2$ photoluminescence at 0.98 eV was performed, as shown in the inset of the figure. Singlet oxygen quantum yields of 35% were obtained for toluene suspensions of the particles. This value correlates well with the diminution of the emission quantum yield due to the presence of oxygen. To clarify the mechanism of the luminescence emission and the O_2 photosensitization, the photophysics of the synthesized particles was thoroughly investigated.

OC22

FORMACIÓN DE HETEROCICLOS DE SELENIO. ESTUDIO FOTOQUÍMICO DE *N*-(SELENOALQUIL)-FTALIMIDAS

<u>Gabriela Oksdath-Mansilla</u>, Adrián A Heredia, Juan E. Argüello y Alicia B. Peñéñory

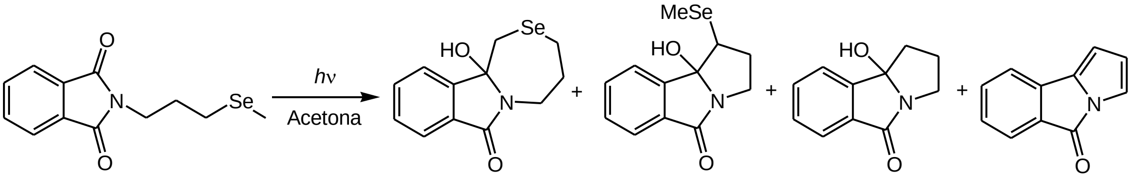
INFICQ, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, penenory@fcq.unc.edu.ar

Palabras Claves: Fotociclización, Fotólisis de Destello Laser, Heterociclos de Selenio.

Durante las dos últimas décadas las reacciones de transferencia de electrón fotoinducidas (TEF) han sido aplicadas con éxito en síntesis orgánica, debido a la alta eficiencia y selectividad observada y a las condiciones suaves de reacción empleadas.[1] Se puede mencionar como ejemplo las fotociclizaciones, que llevan a la construcción de sistemas heterocíclicos que pueden ser dificultosos de sintetizar mediante otros procesos.

El núcleo ftalimida electrónicamente excitado puede participar en una reacción de TE actuando como aceptor de electrones en presencia de un adecuado donador (ya sea en forma inter o intramolecular). En los últimos años se han informado numerosos trabajos que demuestran que las reacciones de fotociclización de ftalimidas *N*-sustituídas pueden ser utilizadas para la síntesis de compuestos heterocíclicos.[2] A diferencia de los conocidos ejemplos en síntesis orgánica de las reacciones de fotooxidación de derivados ftalimidas *N*-sustituidas de azufre y nitrógeno, no se conoce la reactividad de análogos de selenio. Con el objetivo de obtener heterociclos que contengan selenio en su estructura, se estudiaron las reacciones de fotociclización de derivados *N*-(selenoalquil)-ftalimidas.

Para el derivado **1**, se observaron principalmente cuatro productos de fotociclización luego de 24h de irradiación a λ = 300nm en acetona como solvente.



1 2-5mM

2 (8%)

3 (5%)

4 (30%)

5 (< 1%)

Por otro lado se evaluó la dependencia en la eficiencia de la TE con la distancia entre el donador y aceptor de electrones. Se realizó el estudio fotoquímico bajo distintas condiciones de reacción en estado estacionario y mediante técnicas resueltas en el tiempo. Se determinaron los parámetros cinéticos y termodinámicos de modo de dilucidar el mecanismo de reacción.

Referencias

---

[1] (a) Griesbeck, A. G.; Mattay, J. Eds. *Synthetic Organic Photochemistry*, *Molecular and Supramolecular Photochemistry*, Marcel-Dekker: New York, **2005**; Vol 12. (b) Rossi, R. A.; Peñéñory, A. B. *Current Organic Synthesis*, **2006**, *3*, 347-51.

[2].(a) Sato, Y., Nakai, H., Wada, M., Mizoguchi, T., Hatanaka, Y, Migita, Y. and Kanaoka, Y., *Liebigs Ann. Chem.* **1985,** 1099-1118. (b) Coyle, J. D. and Newport, G. L, *J. Chem Soc. Perkin I*, **1980**, 93-96.

OC23

MECHANISM, INTERMEDIATES AND KINETICS OF CHLORONICOTINYL INSECTICIDES WITH ENVIRONMENTAL REACTIVE OXIDANTS

María Laura Dell´Arciprete*, Antonio Arques#, Lucas Santos-Juanes#, Daniel Mártire*, Jorge Furlong§, Mónica Gonzalez*

*INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina, Diag 113 y 64, mlaura@inifta.unlp.edu.ar.
#Departamento de Ingeniería Textil y Papelera., Universidad Politécnica de Valencia, Alcoy, España, Plaza Ferrándiz y Carbonell, s/n 03801.
§Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina, 47 y 115.
Keywords: insecticides, singlet oxygen, triplet state.

Chlronicotinyl insecticides are a new class of pesticides used worldwide for insect pest management during the last decades. Despite their extensive use, only scarce information on the nature of the degradation products and toxicity of neonicotinoid pesticide residues is found in the literature.Imidacloprid(IMD), Thiacloprid(THIA) and Acetamiprid(ACT) were chosen as probes because their chemical structure show a common chloropyridine group and markedly differ on the chemical group responsible for the insecticide toxicity.

Singlet oxygen, O_2 ($^1\Delta_g$), is an important reactive oxidant present in natural aquatic reservoirs. Its generation implies the excitation of a photosensitizer whose lowest energy state (a spin-triplet state) may efficiently transfer their energy to the ground triplet state of oxygen molecules. This higher state of the sensitizer may also initiate the degradation of the insecticides through an initial charge transfer mechanism.

The Rose Bengal triplet quenching by chloronicotinyl insecticides, and the kinetics and mechanisms of singlet oxygen reaction with insecticides are reported herein. The Figure depicts the semilogarithmic plots of the insecticides consumption against photolysis time for experiments in the presence and absence of RB. Singlet oxygen reaction with the insecticides may be explained by a charge transfer pathway leading to the formation of superoxide radical anions, $O_2^{\cdot -}$, and the radical cation of the insecticide in agreement with the reported mechanism for the reaction of $^1O_2$ with substituted amines, involving an α-aminoalkyl radical and its further reaction with molecular oxygen to yield the observed products.

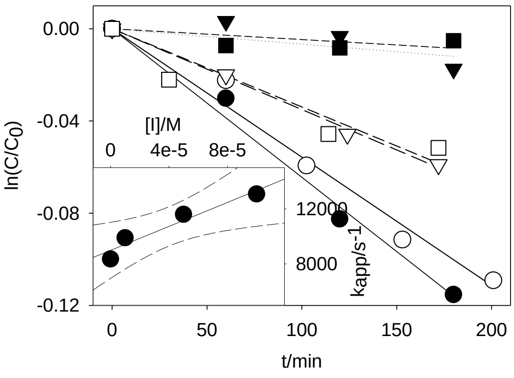


Figure. Logarithmic plot of the relative concentration vs time of IMD (circles), THIA (triangles) and ACT (squares) air-saturated aqueous solutions containing 3.3x10^{-4} M concentration of the insecticides during irradiation with light of λ > 480 nm in the absence (full symbols) and presence (empty symbols) of 10 mg/L of RB. Inset: Plot of k_{app} vs IMD concentration for the decay of RB triplet at 620 nm.

OC24

ESTUDIO DE LA EMISIÓN DE 7,8-DIHIDROPTERINAS EN SOLUCIÓN ACUOSA

Mariana P. Serrano, Mariana Vignoni, M. Laura Dántola, Carolina Lorente y 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: athomas@inifta.unlp.edu.ar

Palabras clave: Fluorescencia, time-correlated single photon counting, pterinas

Las dihidropterinas se encuentran en el organismo cumpliendo diferentes funciones. Los dos derivados más importantes de este grupo son 7,8-dihidroneopterina (H_2Nep) y 7,8-dihidrobiopterina (H_2Bip). H_2Bip es un intermediario en la ruta de reciclado de la tetrahidrobiopterina, la cual actúa como donor de electrones en una serie de reacciones del metabolismo de los aminoácidos.[1] H_2Nep, por su parte, es secretada junto con su análogo oxidado neopterina (Nep) por células del sistema inmune, particularmente por macrófagos activados.[2]

A diferencia de sus análogos oxidados, las dihidropterinas presentan débil emisión de fluorescencia y no generan oxígeno singlete.[3] Se cree que este comportamiento se debe a una eficiente desactivación no radiativa del primer estado excitado singlete (S1). Sin embargo, la caracterización de los estados excitados de estos compuestos es muy compleja por su inestabilidad. En particular, se oxidan fácilmente[4] y, por ende, las contaminaciones con derivados oxidados son inevitables.

En esta contribución presentamos un estudio resuelto en el tiempo de la florescencia de H_2Bip, H_2Nep, 6-metil-7,8-dihidropterina y 6-hidroximetil-7,8-dihidropterina. Se prepararon soluciones acuosas (pH 5,5-7,0) y se analizaron cuantitativamente las impurezas de pterinas oxidadas por Cromatografía Líquida de Alto Rendimiento (HPLC Prominence de Shimadzu). La emisión de las soluciones se analizó en un fluorómetro Horiba Jobin-Yvon que utiliza la técnica Time-correlated Single Photon Counting (TCSPC).

En todos los casos se observaron decaimientos de la emisión biexponenciales con un componente de tiempo de vida (τ_F) corto (< 1 ns), que fue asignado a la dihidropterina estudiada, y un componente de τ_F largo (> 5 ns), que fue asignado a la contaminación del análogo oxidado correspondiente. Mediante análisis global se obtuvieron los valores de τ_F y los espectros de emisión de las dihidropterinas.

1. C. A. Nichol, G. K. Smith and D. S. Duch, *Annu. Rev. Biochem.*, 1985, **54**, 729.
2. C. Huber, J. R. Batchelor, D. Fuchs, A. Hausen, A. Lang, D. Niederwieser, G. Reibnegger, P. Swetly, J. Troppmair and H. Wachter, *J. Exp. Med.*, 1984, **160**, 310.
3. M. L. Dántola, A. H. Thomas, A. M. Braun, E. Oliveros and C. Lorente, *J. Phys. Chem. A*, 2007, **111**, 4280.
4. M. L. Dántola, M. Vignoni, A. L. Capparelli, C. Lorente and A. H. Thomas, *Helv. Chim. Acta*, 2008, **91**, 411-425.

OC25

Photooxidation of $CF_3CCl{=}CCl_2$, $CF_3CCl{=}CClCF_3$ and $CF_3CF{=}CFCF_3$ by OH radicals at 298 K and atmospheric pressure. Atmospheric lifetimes, Ozone Depletion Potentials (ODPs), Radiative Forcings and Global Warming Potentials (GWPs)

Silvina Peirone, Juan Pablo Aranguren, Pablo Cometto, Raúl Taccone, Jorge Nieto,
Silvia Lane

I.N.F.I.Q.C., Depto. de Fisicoquímica- Facultad de Ciencias Químicas, U.N.C. - C.P.
5000, Córdoba, Argentina. E-mail: s-lane@fcq.unc.edu.ar

Keywords: perhalogenated alkenes, OH radical, tropospheric chemistry

Perhaloalkenes are extensively used to synthesize fluoropolymers. A series of hydrocarbons containing both chlorine and fluorine, have been used as refrigerants, blowing agents, cleaning fluids, solvents, and as fire extinguishing agents. Fluorinated alkenes are the most likely reactive impurities in HCFCs, being present as residual starting material from production or as decomposition products. They have been shown to cause stratospheric ozone depletion and have been banned for many uses. It is widely known that, the main gas phase removal process of the volatile organic compounds (VOCs) in the troposphere is photooxidation by OH radicals.

In this work, we present the first experimental determination of the relative rate constants for the reactions of $CF_3CCl{=}CCl_2$, $CF_3CCl{=}CClCF_3$ and $CF_3CF{=}CFCF_3$ with OH at 298 K and atmospheric pressure. The experimental set up used consisted of an 80 L collapsible Teflon film chamber, simulating atmospheric conditions, surrounded by germicidal lamps, providing UV radiation with a λ maximum around 254 nm. These lamps were used to produce OH radicals by the UV photolysis of H_2O_2. The depletion of the organics (perhaloalkenes and reference compounds), by the reaction with OH, was monitored using a gas chromatograph coupled to a flame ionization detector (GC-FID).

The obtained rate constants were: $k(OH + CF_3CCl{=}CCl_2) = (9{,}0 \pm 1{,}1) \times 10^{-13}$, $k(OH + CF_3CCl{=}CClCF_3) = (2{,}1 \pm 0{,}2) \times 10^{-13}$, $k(OH + CF_3CF{=}CFCF_3) = (3{,}7 \pm 0{,}2) \times 10^{-13}$, in units of cm^3 $molecule^{-1}$ s^{-1}. The reference compounds were propane and methanol for $CF_3CCl{=}CCl_2$, acetone and ethane for $CF_3CCl{=}CClCF_3$, and propane and ethane for $CF_3CF{=}CFCF_3$.

Taking into account an OH radical concentration (12 hours daytime average) of 2×10^6 molecules cm^{-3} and the relationship $\tau = 1/k\,[OH]$, the lifetimes of the studied haloalkenes were calculated, obtaining values of 11, 28 and 31 days for $CF_3CCl{=}CCl_2$, $CF_3CCl{=}CClCF_3$ and $CF_3CF{=}CFCF_3$, respectively.

Integrating the absorption cross sections between 500 and 1500 cm^{-1}, radiative forcings for the three compounds were calculated and their GWPs were estimated. ODPs were also calculated.

The obtained ODP values are small, therefore, their impact on the stratospheric O_3 depletion is negligible. On the other hand, The GWP values suggest that these compounds contribute to the greenhouse effect, mainly caused by the strong absorption of the C-F bond in the IR spectral region mentioned above.

OC26

POLYANILINE AND POLY-O-TOLUIDINE PHOTOCHEMICAL SYNTHESIS

Douglas Silva Machado, Tatiana Batista, Carla C. C. Schmitt y Miguel G. Neumann

Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil
machadodouglas@iqsc.usp.br

Keywords: photopolymerization, polyaniline

In this work polyaniline and poly-o-toluidine were photochemicaly synthesized in presence of $AgNO_3$. The polymers were obtained by irradiation of the respective amine (aniline or o-toluidine) with germicide lamps (max. emission 254 nm) in acid medium. The UV-vis spectrum of the mixture of amine and acid is dependant of the concentration of acid and $AgNO_3$, explaining why no polymerization was observed with visible light. The mechanism of the photopolymerization is here explained based in the oxidation of aniline leading to the formation of the radical anilinium by absorption of light, as observed by flash photolysis. The radical anilinium is known to be the precursor of the formation of polyaniline chain, in the chemical and the electrochemical via of synthesis. Instead of the formation of the anilinium radical by irradiation of the mixture aniline/acid, no polymerization was observed without adding $AgNO_3$. The salt is believed to act as an electron acceptor, restricting the recombination of the solvated electron and the ionized amine. The reduced Ag is visualized in scanning electron microscopy (SEM) as a crystal. SEM confirms also the very well known morphology for polyaniline, as well as UV-vis spectra of the polymer dissolved in n-methyl pirrolidone.

The authors thank CNPq, Capes and FAPESP for financial support.

OC27

TRIPLET STATE ENERGY OF THE HUMIC SUBSTANCES DETERMINED BY PHOTOACOUSTIC CALORIMETRY

Marcela Martin,[1†] **Ricardo Mignone,**[2] **Mónica Gonzalez,**[1] **Daniel Mártire,**[1] **Claudio Borsarelli** [2]
[1]INIFTA, UNLP. La Plata, Argentina. Diagonal 113 y 64, CP. 1900
[2]INQUINOA, UNSE. Santiago del Estero, Argentina. Av. Belgrano (S) 1912, CP. 4200
[†]Email: marcemartin84@gmail.com

Key words: humic substances, triplet states and radical cations.

In this communication we performed Laser-Induced Optoacoustic Spectroscopy (LIOAS) experiments with Aldrich Humic Acid (AHA), Pony Lake (PLFA) and Waskish Peat (WPFA) Fulvic Acids (FA) to obtain information on the properties of long-lived species formed after irradiation with light of humic substances (HS).

Results

Figure 1 shows the optoacoustic signals of the calorimetric reference $K_2Cr_2O_7$ and AHA 20 mgL^{-1} in 75 mM phosphate buffer solutions, pH 7.47 at 19.3ºC.

Humic Substance $E_{\lambda 355nm}$ 80,5 kcal.mol^{-1}	$E_\lambda = \alpha E_\lambda + E_F\Phi_F + E_{st}\Phi_{st}$				
	α	$\alpha E_{\lambda 355nm}$ kcal.mol^{-1}	$E_F\Phi_F$ kcal.mol^{-1}	$E_{st}\Phi_{st}$ kcal.mol^{-1}	Φ_{st}
AHA (pH 4.08**)**	0.953±0.009	76.7	0.175	3.63	0.09
AHA (pH 10.97**)**	0.948±0.008	76.3	0.990	3.21	0.08
PLFA (pH 2 /Ar**)**	0.938±0.009	75.5	0.788	4.21	0.11
PLFA (pH 2 /O_2**)**	0.891±0.007	71.7	0.701	8.10	0.21
WPFA (pH 2 /Ar**)**	0.921±0.009	74.1	0.341	6.06	0.16
WPFA (pH 2 /O_2**)**	0.934±0.008	75.2	0.320	4.98	0.13

Table 1: Parameters derived from the Energy balance from LIOAS and fluorescence experiments.

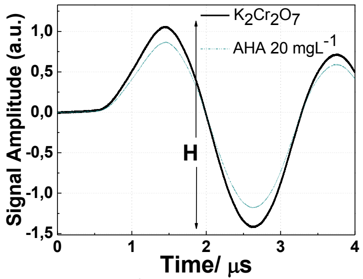


Figure 1

Table 1 shows that: (i) about 92-95 % of the absorbed energy is released as prompt heat, (ii) a very small fraction (< 0.3 %) is emitted as fluorescence and, (iii) about a 4 % of the absorbed energy is stored by long-lived transients.

Conclusion

The species which stores the energy in the LIOAS experiments could be triplet states or radical cations of the HS formed from the triplet states. The calculated energy content for the lowest excited triplet state of the buffle model is 38 kcal mol^{-1}. This value is very close to that reported (1, 2) for fulvic acids (41-43 kcalmol^{-1}) and can be taken as an upper limit of E_{st}. Taking E_{st} = 38 kcal mol^{-1} and the values of $\mathbf{E_{st}\Phi_{st}}$ obtained from the optoacoustic experiments, $\mathbf{\Phi_{st}}$ was calculated (see Table 1). The values of $\mathbf{\Phi_{st}}$ are on the order of those reported for the primary quantum yields of formation of the solvated electrons (2), which supports the assignment of the energy-storing species to the radical cation.

References

1. Bruccoleri, A., Langford C.H., Arbour, C.. Environ. Technol. Lett., **11**, Issue 2, 169–172 (1990)
2. Bruccoleri, A., Bhuvan C. Pant, Devendra K., Sharma, Cooper H. Langford. Environ. Sci. Technol., **27**, 889-894 (1993)

POSTERS PRESENTATIONS

P1

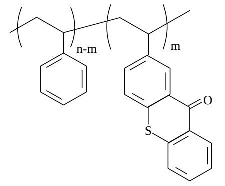
ESTUDO POR FOTÓLISE POR PULSO DE LASER DE MACROFOTOINICIADORES CONTENDO TIOXANTONA

Leticia Felipe Abdias Pinto[1], Beatriz Eleutério Goi[2], Miguel Guillermo Neumann[1], Carla Cristina Schmitt Cavalheiro[1]

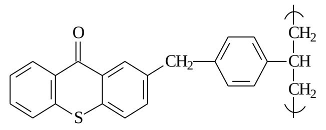
[1]Instituto de Química de São Carlos, Universidade de São Paulo, Departamento de Físico-Química (DFQ), São Carlos, Brazil, leticia_fap@iqsc.usp.br
[2]Faculdade de Ciências e Tecnologia, Universidade Estadual Paulista "Júlio de Mesquita Filho", Departamento de Física, Química e Biologia (DFQB), Presidente Prudente, Brazil, beatriz_goi@fct.unesp.br

Palavras-chave: fotólise por pulso de laser, macroiniciadores, tioxantona.

Macrofotoiniciadores, que são macromoléculas contendo grupos fotoiniciadores pendentes ligados covalentemente, tem sido alvo de numerosos estudos já que oferecem vantagens sobre os fotoiniciadores de baixo peso molecular, como por exemplo, baixa migração devido ao efeito polimérico e também baixa reatividade. No presente trabalho foram investigadas a supressão dos macrofotoiniciadores PS-TX I e PS-TX II em diferentes solventes. O estudo de supressão de triplete por trietanolamina (TEOHA) foi realizado através da técnica de fotólise por pulso de laser utilizando-se para excitação um laser de Nd-YAG com comprimento de onda de excitação em 355 nm e a absorção do triplete-triplete (*T*-*T*) nos diferentes solventes foi monitorada em 660 nm. A constante de velocidade de supressão (k_q) para a desativação do triplete de PS-TX II diminuiu com o aumento da polaridade do solvente seguindo assim o mesmo comportamento apresentado pelos sistemas com tioxantona livre; o mesmo não foi observado para o macrofotoiniciador PS-TX I. Tal resultado é coerente quando se compara a estrutura de PS-TX I, PS-TX II e a tioxantona livre. Já os macrofotoiniciadores PS-TX I em tetrahidrofurano e PS-TX II em dimetilformamida apresentaram valores de constantes de velocidade de supressão menores que 10^9 (L.mol^{-1}.s^{-1}), diferentemente dos valores encontrados para a tioxantona livre (ordem difusional). Este comportamento pode estar relacionado com os solventes utilizados e com as diferenças estruturais entre PS-TX I, PS-TX II e a tioxantona livre. A tioxantona incorporada em uma estrutura polimérica torna a difusão mais lenta, ou seja, o encontro entre a amina e a TX é dificultada, diminuindo assim o valor da constante de velocidade de supressão (k_q). **Agradecimentos:** FAPESP e CNPq pelo apoio financeiro e ao Dr. Fernando Catalina (Instituto de Ciencia y Tecnología de Polímeros, Madri, Espanha) pelo macrofotoiniciador PS-TX II.



PS-TX I



PS-TX II

P2

ESTUDOS DAS PROPRIEDADES FOTOQUIMICAS DO COMPLEXO *fac*-$[Mn^{I}(CO)_3(phen)(4MeImH)]^+$ E SUA APLICAÇÃO EM REAÇÕES DE TRANSFERÊNCIA DE ELÉTRONS

Inara de Aguiar*, Simone D. Inglez*, Rose M. Carlos*
*Departamento de Química, Universidade Federal de São Carlos, São Carlos, Brasil.
inara@dq.ufscar.br

Palavras chave: transferência de elétrons, manganês (I), foto-catálise

As alterações estruturais que ocorrem em muitos complexos de metais de transição, induzidas por reações de transferência de elétrons (TE) são fundamentais para a elucidação de alguns mecanismos de reações que ocorrem em processos naturais, como por exemplo, a fotossíntese. Neste contexto, os complexos de metais de transição apresentando transições eletrônicas de transferência de carga do tipo metal para ligante (MLCT) podem participar de processos de transferência de elétrons e de energia.

O complexo *fac*-$[Mn^{I}(CO)_3(phen)(4MeImH)]^+$ apresenta estados de transferência de carga de menor energia $Mn(3d_{t2g}) \rightarrow phen(\pi^*)$, exibindo uma banda no espectro de UV-vis em 380 nm (ε = 3200 $mol.L^{-1}.cm^{-1}$). Suas propriedades espectroscópicas são alteradas em diferentes solvente (CH_2Cl_2, CH_3CN, H_2O e D_2O) e também na presença de sais (TBAP, CH_3COONa, KH_2PO_4). Quando o complexo *fac*-4meim, em CH_2Cl_2, é irradiado com luz contínua de 350 nm, observa-se a formação de uma nova espécie em 550 nm. Em solução aquosa ocorre à formação de novas bandas em 405, 512, 638 e 758 nm e a solução que inicialmente é amarela torna-se avermelhada após cerca de 60 segundos de irradiação, e posteriormente esverdeada com liberação de bolhas. O espectro de UV-vis obtido após 120 segundos de fotólise é característico de compostos de manganês com altos estados de oxidação, tendo pontes do tipo μ-oxo, sugerindo que o complexo apresente processos oxidativos sucessivos durante a fotólise ($Mn^{I} \xrightarrow{h\nu} Mn^{II} \rightarrow Mn^{II}/Mn^{III} \xrightarrow{h\nu} Mn^{III}/Mn^{IV}$). O espectro de RMN de ^{1}H do *fac*-4meim revelou a existência de dois isômeros, adjacente e remoto, após 60 segundos de fotólise nota-se uma redução de 80% no isômero remoto e há a formação de novas espécies.

A habilidade para realizar reações de transferência de elétrons foi confirmada através da fotólise do *fac*-4meim na presença de MV^{2+}, um receptor de elétrons que apresenta bandas características no espectro de absorção quando reduzido. A presença de oxigênio foi detectada espectroscopicamente usando como detector o ácido pirogálico e também eletroquimicamente utilizando micro eletrodos de Clark.

Estes estudos demonstram a viabilidade em utilizar este complexo para atuar em reações de transferência de elétrons similares àquelas ocorridas no PSII, no processo de fotossíntese natural.

P3

EFFECT OF NA,K-ATPase REINCORPORATED INTO GUV´s MODELS UPON SEGREGATION DOMAINS: STUDY BY TWO PHOTON MICROSCOPY

Luis F. Aguilar[&], Francisco Cuevas[#], Carlos P. Sotomayor[&], Marco Soto-Arriaza* and Susana Sanchez[§]

[&] Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile, Av. Parque Sur 320, Curauma. laguilar@ucv.cl; psotomay@ucv.cl

[#]Departamento de Ciencias Básicas, Universidad Santo Tomás, Av. Limonares 190, Viña del Mar, fcuevasc@ust.cl
*Departamento de Química-Física, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile, Av. Vicuña Mackenna 4860, Macul, marcosoto@uc.cl
[§]Laboratory for Fluorescence Dynamics, Department of Biomedical Engineering, University of California-Irvine, Irvine CA. susanas@uci.edu

Key words: Macrodomains, Two Photon image, Generalized Polarization

In the present work, we study the effect of Na,K-ATPase in lipid segregated domain when it is incorporated into giant unilamellar vesicles (GUV´s) formed by DPPC:DOPC lipid mixture in absence and presence of different content of cholesterol. The result was obtained measuring GP Laurdan image. The protein reconstitution into GUV´s was realized by adapting Cornelius methods. This reconstitution was realized through incubation of protein previously solubilized with lipid:detergent solution at 1:1,2 ratio. After that, detergent was removed by hydrophobic polystyrene polymer (Bio-Beds™) when the lipid solution was maintained for 12 hr at 4°C to constant stirrer.

LUVs of reconstituted Na^+,K^+-ATPase into different lipid-cholesterol mixtures to grow the Giant Unilamelar Vesicles using the conventional electroformation method with some modifications to avoid the dehydration of the protein. In the presents work, we used Two-photon microscopy to obtain Laurdan GP imaging to study membrane segregated domains. Laurdan [6-lauroyl-2-(dimethylamino) naphthalene] is used as a membrane probe because of its large excited-state dipole moment, which results in its ability to report the extent of water penetration into the bilayer. Water penetration has been correlated with lipid packing and membrane fluidity according.

According to our result, for DPPC:DOPC lipid mixture, in absence and in presence to 20 mol% of cholesterol, was observed lipid phase separation from 37°C approximately. On the other hand, for lipid mixture without and in presence of 15 mol% of cholesterol and in presence of protein reincorporated, was observed lipid phase separation a slightly lower temperature (32°C). But, for lipid mixture in presence of 20 mol% cholesterol, we does not observed lipid phase separation. In relation to our result, is important to note that the lipid mixture with 30 and 40 mol% of cholesterol, in absence and in presence of reincorporated protein, was not observed lipid phase separation in range temperatures studied. In order to established whether the protein is principally distributed into ordered or disordered domain, Na^+,K^+-ATPase was marked with FITC fluorescent probe. Two photon microscopy images were obtained. According our result, the protein does not present preferential placement in any lipid mixture in which there were lipid domain.

Acknowledgements: This work was supported by FONDECYT, project 1070320 and NIH, Grant PHS 5 P41 RR-03155, US

P4

CARACTERIZACION DE NANOCOMPOSITOS Ag@ZnO POR ESPECTROSCOPIA DE ABSORCIÓN Y EMISIÓN

Matías E. Aguirre,* Hernán B. Rodríguez,# Enrique San Román# y María A. Grela*

*Dpto de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata Funes 3350. Mar de Plata, Argentina, meaguirre@mdp.edu.ar
INQUIMAE / DQIAyQF, Facultad de Ciencias Exactas y Naturales, UBA, Ciudad Universitaria, Pab II, C1428EHA, Buenos Aires Argentina, hbr@qi.fcen.uba.ar.

Palabras clave: Nanocompositos metal semiconductor, plata, óxido de zinc.

El diseño de nanocompositos del tipo nucleo@cubierta constituidos por un metal noble y un semiconductor es un área activa de investigación impulsada por la posibilidad de obtener materiales con propiedades ópticas y electrónicas superiores a los componentes individuales que encuentran aplicación en el desarrollo de sensores, dispositivos optoelectrónicos, celdas solares , marcadores biológicos y fotocatalizadores.

Las condiciones de la síntesis determinan en gran medida las propiedades finales de los nanocompositos. La estrategia propuesta en este trabajo consiste en la formación simultánea del metal (Ag) y el óxido (ZnO) en dimetilformamida. Este solvente provee a la vez el medio reductor necesario para la transformación de Ag^+ en Ag^0 y un medio alcalino controlado para la hidrólisis del precursor del semiconductor (acetato de zinc).

La formación de Ag@ZnO es evidenciable por espectroscopia UV-Vis y da lugar a un corrimiento batocrómico en el plasmón de la Ag de aproximadamente 30 nm, debido al cambio dieléctrico en el entorno de las partículas metálicas. Los nanocompositos pueden ser fácilmente dispersados en distintos solventes y su estabilidad depende de la relación molar porcentual de los precursores ($R = n_{Ag^+} / n_{AcZn} \times 100$).

Los espectros de emisión poseen una banda en el UV centrada en 360 nm y una banda visible muy ancha que se extiende entre 400 y 800 nm. El análisis de los espectros con valores de R entre 5 y 40, muestra que la presencia del metal afecta no solo la intensidad de la emisión sino también la forma del espectro, indicando que la misma está dada por recombinaciones radiativas derivadas de distintos intermediarios. Para R menor que 7 y a medida que aumenta el contenido de Ag, se observa el quenching de una emisión centrada en 540 nm y la desaparición de la banda en el UV. Por encima de R = 10 se completa el quenching de la emisión de esta banda y comienza a evidenciarse la disminución de otra centrada en 620 nm que va acompañada de un aumento en la emisión UV.

Por otra parte, los espectros de excitación a las longitudes de onda correspondientes a las bandas observadas indican que las mismas derivan de especies diferenciadas y sugieren la presencia de clusters de distinto tamaño. Este comportamiento se observa también para R = 0, por lo que se concluye que las propiedades emisivas están determinadas por el medio reductor usado en la síntesis, observándose marcadas diferencias con las observadas para el ZnO sintetizado vía hidrólisis alcalina en alcohol (usada en la literatura como estándar).

P5

PHOTOPHYSICAL CHARACTERIZATION OF ATORVASTATIN (LIPITOR®) ORTHO-HYDROXY METABOLITE: ROLE OF HYDROXYL GROUP ON THE DRUG PHOTOCHEMISTRY

Emilio Alarcón,[a] María González-Béjar,[a] Serge Gorelsky,[a] Roberto Ebensperger,[b] Camilo Lopez-Alarcón,[b] José Carlos Netto-Ferreira [a,c*] and Juan C. Scaiano[a].

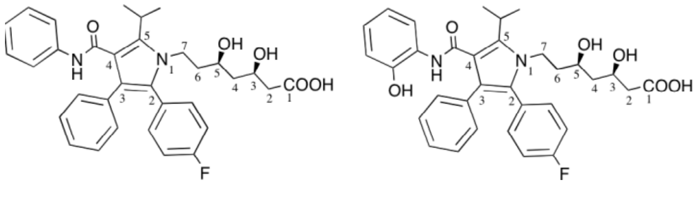
[a] Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario, K1N 6N5.

[b] Departamento de Farmacia, Facultad de Química, Pontificia Universidad Católica de Chile. C.P. 782 0436, Santiago, Chile.

[c] Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Antiga Rio-São Paulo km 47, Seropédica, 23851-970, Rio de Janeiro, Brazil.

Key Words: Atorvastatin, ortho-hydoxy-metabolite, hydrogen abstraction and energy transfer.

We have evaluated the influence of phenolic hydroxyl group on the photophysical and photochemical behavior of the most abundant Atorvastatin (Ato) metabolite: *ortho*-hydroxy atorvastatin metabolite (Ato-OH) by using steady and time resolved experiments. Both compounds after 266 nm laser excitation produced the phenanthrene-like intermediate formation, being ~ 30% for Ato-OH less efficient than that for its parent compound in methanol. Additionally, Ato and Ato-OH were efficient quenchers for benzophenone (E_T~69 Kcal/mol) and xanthone (E_T~74 Kcal/mol) triplet excited states with rate constants close to diffusion limit control. These results suggest that energy transfer mechanism is taking place, since the lower triplet energy for Ato and Ato-OH was found ~ 63 Kcal/mol and π,π* character as revealed from DFT calculations. Interestingly, only Ato-OH was able to act as a hydrogen donor towards benzil triplet excited state (E_T~54 Kcal/mol) due to the presence of the phenolic hydroxyl group. Nevertheless, the presence of this group in Ato-OH does not modify significantly the compound reactivity toward singlet oxygen. The importance of triplet energy transfer in biological systems to form Ato and Ato-OH triplet excited state as well as the hydrogen donor capacity of Ato-OH toward triplet excited state are discussed in the present contribution.



Chemical structure of Ato (left) and its ortho-hydroxy metabolite (rigth).

Acknowledgments: The Natural Sciences and Engineering Research Council (NSERC, Canada). The authors express thanks to Pfizer for supplying Atorvastatin and its metabolite.

P6

MARCACIÓN ISOTÓPICA SELECTIVA EN DERIVADOS DE BENZOPERIMIDINAS

Christian Aliaga, **Claudio Saitz, Carolina Jullian, Julio de la Fuente.**

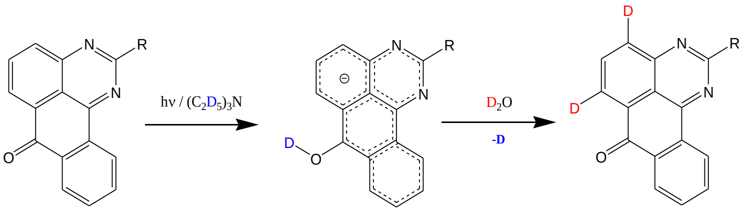
Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile. Casilla 233, Santiago 1, Chile, e-mail: c.aliaga@ciq.uchile.cl, jrfuente@ciq.uchile.cl

Palabras clave: intercambio isotópico, fotorreducción, benzoperimidinas.

Las benzoperimidinas han sido estudiadas como agentes antineoplásicos para el tratamiento del cáncer, con efectividad contra resistencia multidroga (MDR), baja actividad peroxidativa y menor cardiotoxicidad.[1]

La 7H-benzo[e]perimidin-7-ona (R: H) y 2-metil-7H-benzo[e]perimidin-7-ona (R: CH_3), en ausencia de oxígeno, fotorreducen eficientemente en presencia de aminas terciaria, como trietilamina (TEA) o tripropilamina (TPA). La fotorreducción ocurre a través de un mecanismo secuencial de transferencia de electrón-protón-electrón, formando el anión hidrogenado del sustrato. Este fotoproducto metaestable revierte lentamente al compuesto original al almacenar la solución fotolizada en la oscuridad y rápidamente al admitir oxígeno en el medio, como se ha observado en sistemas similares.[2]

El intercambio isotópico observado, en las posiciones 4 y 6 de las benzoperimidinas, se explica a través de una sustitución electrofílica aromática sobre el anión fotoproducto, en presencia de agua deuterada. Este proceso de intercambio isotópico permitiría introducir deuterio o tritio selectivamente en las posiciones mencionadas para estudios bioquímicos de agentes antineoplásicos derivados de benzoperimidinas.



R = H; -CH_3

Referencias:

1.- (a) Bu, X., et. al., Bioorganic & Medicinal Chemistry, 2005. 13(11): p. 3657-3665. (b) Glowacka-Rogocka, D., et. al., Cancer Detection and Prevention, 2004, 28: p. 283-293. (c) Dzieduszycka, M., et. al., Bioorganic & Medicinal Chemistry, 2002. 10: p. 1025-1035. (d) Stefanska, B., et al., Journal of Medicinal Chemistry, 1999. 42: p. 3494-3501.

2.- De la Fuente, J., et. al., J. Phys. Chem. A, 2009, Publicación Aceptada; J. Phys. Chem. A, 2008, 112, 10168-10177; J. Phys. Chem. A, 2005, 109, 5897-5904; Photochem. Photobiol. Sci., 2004, 3, 194-199.

Agradecimientos: CA agradece a CONICYT por beca de estudio de Doctorado y beca de apoyo a la realización de tesis N° 24091001. JDLF agradece a FONDECYT N° 1070623.

P7

EFFECT OF HYDROPHOBICITY OF TEMPO-DERIVED PREFLUORESCENT PROBES ON THE RATE CONSTANT OF HYDROGEN ABSTRACTION WITH ANTIOXIDANTS

Carolina Aliaga, Cristián Tirapegui and Marcos Caroli

Facultad de Química y Biología, Universidad de Santiago de Chile
carolina.aliaga@usach.cl

The participation of free radical processes in biological systems is a subject of permanent interest. In these environments, the observed antioxidant activities are expected to depend on the location of the antioxidant and the attacking radical in the microheterogeneous systems.

We have recently proposed the use of nitroxide prefluorescent probes to evaluate hydrogen-transfer-rate constants from highly reactive polyphenols in homogeneous media. Our method was based on the ability of a tethered TEMPO unit to quench intramolecularly a fluorescent chromophore. The abstraction of a hydrogen atom from the antioxidant by the TEMPO nitroxide generates a diamagnetic hydroxylamine, thereby restoring the chromophore fluorescence.

In this work we describe the use of new prefluorescent probes obtained by attaching a TEMPO unit to chromophores based on pyrilium and xanthenium salts. These systems have been used in homogeneous and micellar systems to evaluate antioxidant efficiency. The system takes into account both the antioxidant and the attacking radical hydrophobicities and their partition in a microheterogeneous medium.

P8

PROPIEDADES FOTOFÍSICAS Y FOTOQUÍMICAS DE COLORANTES XANTENICOS UNIDOS COVALENTEMENTE A QUITOSANO

María E. Andrada, José Natera, Norman A. García y Walter A. Massad

Departamento de Química, UNRC, Río Cuarto, Argentina
email: wmassad@gmail.com

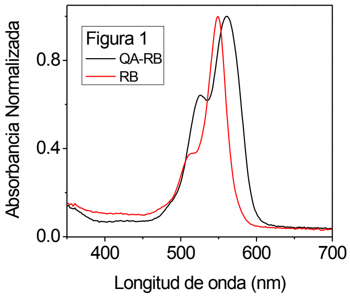
Palabras clave: colorantes xanténicos, oxígeno singlete, quitosano.

Los colorantes poliméricos (CP) presentan algunas propiedades que los muestran como interesantes desde el punto de vista fisicoquímico. Permiten controlar el entrono del colorante, moldearlo, fraccionarlo y emplearlo formando mezclas heterogéneas sólido-líquido, para retirarlo mecánicamente a voluntad.

Hemos sintetizado dos CP y estudiado la fotoquímica y fotofísica de los mismos. Ellos fueron los colorantes xanténicos (Xa) eosina (Eo) y rosa de bengala (RB) unidos covalentemente a quitosano (QA), que llamamos respectivamente QA-Eo y QA-RB. El QA es un copolímero lineal de β(1-4) 2-acetamido-2deoxi-β-D-glucopiranosa (N-acetil glucosamina) y 2-amino-2-deoxi-β-D-glicopiranosa (glucosamina). Es fácilmente obtenido a partir de la quitina y constituye el segundo polímero natural más abundante, luego de la celulosa [1].

Los CP se sintetizaron tomando como base a los trabajos de Mansuri *et al.*[2] y Campos *et al.*[3], lográndose la unión QA-Xa a través de un enlace amida.

En ambos CP se observó un corrimiento batocrómico en los máximos de los espectros de absorción y emisión de fluorescencia como se observa en la Fig. 1 para QA-RB. Además se determinaron los rendimientos cuánticos de emisión de fluorescencia, que en ambos casos resultaron menores que los valores de los Xa en agua . Mediante la técnica de conteo de fotón único se determinó el tiempo de vida de fluorescencia de los CP y de los Xa en solución, resultando sustancialmente mayores los de los compuestos poliméricos.



Los espectros de especies transitorias de los CP, determinados en ausencia de oxígeno en la ventana temporal del microsegundo, muestran diferencias con los datos de literatura publicados para los Xa en solución.

Experimentos empleando consumo de O_2 demostraron que ambos CP son capaces de generar la especie oxígeno singlete molecular ($O_2(^1\Delta_g)$) e incluso se evaluó, con resultados positivos, la posibilidad de empleo de los CP mencionados como fotosensibilizadores para la fotodegradación por luz natural de contaminantes acuáticos transparentes a la radiación visible.

Discutimos de manera conjunta el origen de las diferencias halladas entre las propiedades fotoquímicas de los CP y los Xa y el empleo de los primeros en acciones de fotoquímica sustentable.

(1) Ausar, S. F. Estudio de la Interacción entre Polímeros Catiónicos y Sistemas Coloidales de Proteínas. Doctoral, Universidad Católica de Córdoba, 2002. (2) Mansouri, S.; Cuie, Y.; Winnik, F.; Shi, Q.; Lavigne, P.; Benderdour, M.; Beaumont, E.; Fernandes, J. C. *Biomaterials* **2006**, *27*, 2060. (3) De Campos, A.; Diebold, Y.; Carvalho, E.; Sánchez, A.; José Alonso, M. *Pharm. Res.* **2004**, *21*, 803.

P9

PHOTOPYSICAL PROPERTIES OF BIFLAVONOIDS OF CAESALPINIA PYRAMIDALIS

Willian Andrade Prado, Marcus Vinícius Bahia and Jacques Antonio de Miranda

Instituto de Ciências Ambientais e Desenvolvimento Sustentável, Universidade Federal da Bahia, Barreiras, Brasil, R. Prof. José Seabra s.n., jacques.miranda@ufba.br

Key Words: *Caesalpinia pyramidalis,* biflavonoids, biopolymer

Caesalpinia pyramidalis is a tree belongs to the family Leguminosae-Caesalpinoideae, endemic in the northeastern Brazilian region that predominates as the caatinga vegetation. Recently we have isolated 20 compounds, especially flavonoids and biflavonoids from this plant [1-3]. Some biflavonoids have been studied by our research group, focusing on assessing the interaction between natural compounds and different means of dispersal, seeking industrial and pharmaceutical applications.

In this study, we evaluated the photophysics using absorption and fluorescence spectroscopy of agathisflavone (CP10), podocarpusflavone A (CP11) and loniflavona (CP12) in different solvents and biopolymers (amylopectin and carboxymethylcellulose).

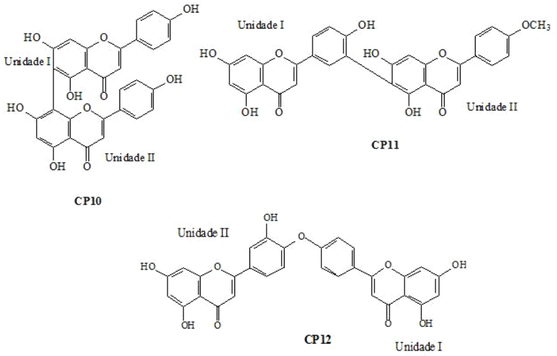


Fig.1. Biflavonoids studied.

The data show a trend bathochromic shift of both the wavelengths of absorption and emission, as it changes the polarity of the solvent. The estimates for the Stokes shifts suggest that the excited state species is less polar than the ground state. The bathochromic shift of the absorption bands in DMF show occur deprotonation of the hydroxyls of the flavonoids, modifying the chromophore and hence the fluorophore. We observe the viscosity effect on the fluorescence emission in alcohols. By analyzing the fluorescence quantum yields, observing the sequence, water-methanol-ethanol-propanol-butanol-ethylene glycol, there is a dependency property photophysics according to the medium viscosity. The same behavior is observed both in amylopectin and carboxymethylcellulose. It is worth noting also that the highest estimated values for the quantum yields of fluorescence were observed in biopolymer solutions.

[1] Mendes, C.C., Bahia, M. V., David, J. M., David, J.P. *Fitoterapia*, **2000**, 71, 205-207.
[2] Bahia, M.V.; Batista, J. S.; David, J.M.; David, J.P. *J. Braz. Chem. Soc*. **2005**, 16, 1402.
[3] Bahia, M.V. Tese de Doutorado, Universidade Federal da Bahia, 2007

P10

MOVIMIENTOS LOCALES EN PELÍCULAS POLIMÉRICAS DELGADAS

Beatriz Aráoz*, Jennifer Faust[#], Pedro Aramendia[*]

**INQUIMAE y DQIAyQF. FCEN. UBA. Pab 2. Ciudad Universitaria. C1428EHA. Buenos Aires. E-mail: beatriz@qi.fcen.uba.ar*

[#] Illinois Wesleyan University, Department of Chemisty. Bloomington, IL. USA.E-mail: jfaust@iwu.edu

***Palabras claves**: Nanoconfinamiento, Transición vitrea, REES.*

La emisión de sondas fluorescentes es altamente sensible al entorno en el que se encuentra. En polímeros amorfos, debido a su rigidez, existen entornos diferentes para una sonda fluorescente que dan origen a una distribución de energías de interacción sonda-polímero. La emisión por excitación en el flanco rojo del espectro de absorción (REES) selecciona moléculas que absorben energía desde niveles vibracionales por encima del nivel vibracional más bajo del estado fundamental. Esto da origen a una *fotoselección de sitios*, causada por energías diferentes. Este efecto es fuertemente dependiente del tiempo de reorganización del medio y se observa preferentemente en sistemas con baja movilidad estructural. En polímeros amorfos, por debajo de la T_g, los entornos no llegan a equilibrarse en el tiempo de vida del estado excitado y el REES es apreciable. Se observa entonces, un desplazamiento del espectro de fluorescencia hacia longitudes de onda mayores respecto de la excitación en el máximo de absorción. Por encima de la T_g la movilidad del medio aumenta, los entornos pueden equilibrarse y el sistema puede reorganizarse disminuyendo considerablemente el corrimiento del espectro. Alrededor de T_g se produce un gran aumento de la movilidad a escala atómica y la longitud típica de correlación de estos movimientos crece rápidamente. Varios estudios indican que la T_g de películas poliméricas puede variar con el espesor cuando éste se encuentra entre los 10 y 500 nm. Experimentalmente se realizaron medidas de excitación y de emisión de fluorescencia en estado estacionario en función de la temperatura y longitud de onda de excitación (510 nm y 540 nm) para la sonda Rojo Nilo (RN) embebida en películas de poli(metacrilato de n-butilo) PBMA; poli(metacrilato de n-propilo) PPMA; poli(metacrilato de etilo) PEMA y poli(metacrilato de metilo) PMMA de 350 µm, 200nm, 100 nm, 50 nm y 25 nm de espesor, obtenidas por spin-coating. Se observaron efectos de solvatocromismo, termocromismo y REES. En todos los polímeros se observó un aumento de la amplitud del corrimiento espectral en espesores menores de 50 nm. Las películas de 350 µm, 200 nm y 100 nm tienen comportamiento similar, lo cual podría estar indicando que no existen efectos de nanoconfinamiento a esta escala. El máximo de emisión a 510 nm se desplaza hacia el rojo con la disminución del espesor, llegando hasta $\Delta\lambda_{em}$=18 nm para espesores de 25 nm con respecto a películas gruesas. Esto indica un aumento de la polaridad con la disminución del espesor. Este corrimiento al rojo es paralelo a un incremento en la variación del efecto REES con la temperatura.

Por encima de la T_g un aumento de la temperatura no tiene efecto sobre el REES.

P11

GENERACIÓN FOTOQUÍMICA DE RADICALES ORGÁNICOS COVALENTEMENTE LIGADOS A NANOPARTÍCULAS DE SÍLICE

Valeria B. Arce[1,2], Sonia G. Bertolotti[3], Mónica C. Gonzalez[1], Patricia E. Allegretti[2] y Daniel O. Mártire[1]

[1] INIFTA, U.N.L.P., Casilla de Correo 16, Sucursal 4, (1900) La Plata, Argentina.
[2] LADECOR, Depto de Química, Facultad de Ciencias Exactas, U.N.L.P., Argentina.
[3] Departamento de Química, U.N.R.C., 5800 Río Cuarto, Argentina.
E-mail: varce@quimica.unlp.edu.ar

Palabras clave: Fosforescencia, nanopartículas, safranina

En este trabajo se realizaron experimentos de láser flash fotólisis (l^{exc} = 532 nm) en los que se generaron tripletes de safranina-T en acetonitrilo (l max = 825 nm) en ausencia y presencia de nanopartículas de SiO_2 modificadas con alcohol 4-metoxibencílico (NP3) alcohol 4-N,N-dimetilbencílico (NP4). En estos experimentos se observó que: (1) el decaimiento del triplete de safranina se acelera en presencia de las nanopartículas y (2) a partir del decaimiento del triplete se forma una especie con máximo de absorción alrededor de 680 nm, que puede atribuirse a radicales orgánicos (ver la figura para NP4).

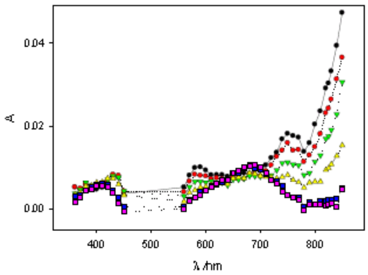
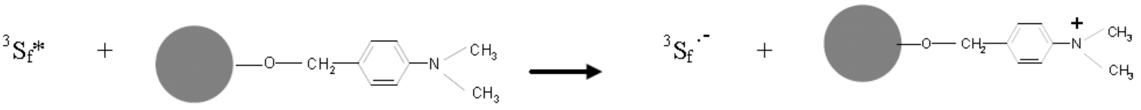


Figura: Espectros de absoción a diferentes tiempos para el triplete de la safranina-T en presencia de NP4



Para asignar los radicales orgánicos observados se realizaron experimentos comparativos en los que los quenchers empleados fueron los alcoholes utilizados en la funcionalización de las nanopartículas.

P12

EFECTO DE LA ATRACCION ELECTROESTATICA ENTRE LISOZIMA Y ALBUMINA DE SUERO HUMANO EN LA FORMACION DE ENTRECRUZAMIENTOS COVALENTES, FOTOINDUCIDOS POR AZUL DE METILENO Y RIBOFLAVINA.

Andrea Arenas[1], Rodrigo Vasquez[1], Eduardo Lissi[2], Camilo López[1] y Eduardo Silva[1]

Facultad de Quimica, Pontificia Universidad Catolica de Chile, Santiago 6094411, Chile,
esilva@uc.cl

Palabras claves: Fotosensibilización, uniones intermoleculares, lisozima-HSA.

Las proteínas cristalinas del lente ocular se caracterizan por una alta sensibilidad a formar entrecruzamientos covalentes en procesos fotosensibilizados. Este particular comportamiento ha sido atribuido a la proximidad que existe entre las cristalinas, que están organizadas en estructuras multiméricas de alto peso molecular. En este trabajo y con la finalidad de validar el supuesto anterior, se estudió un modelo simple constituido por dos proteínas globulares monocatenarias, lisozima (Lys, pI= 11) y albúmina de suero humano (HSA, pI= 4,7) las cuales, a pH= 7,9, coexisten en su forma catiónica y aniónica respectivamente. Se estudió primeramente el comportamiento fotoquímico de estas dos proteínas en forma independiente, empleando altas concentraciones de estas, utilizando azul de metileno (MB) y riboflavina (RF) como sensibilizadores. Los rendimientos cuánticos para la formación de dímeros Lys-Lys y HSA-HSA fueron mayores cuando se utilizó RF como sensibilizador, siendo el entrecruzamiento fotoinducido Lys-Lys más eficiente que el HSA-HSA. Considerando que RF es preferentemente un sensibilizador de Tipo I y MB es mas bien de Tipo II, se procedió también a estudiar el entrecruzamiento entre estas proteínas inducido por los radicales libres generados a partir de la termólisis de AAPH (diclorhidrato de 2,2´-azobis(2-amidinopropano). Se realizó un estudio comparativo entre ambos procesos de entrecruzamiento. Cuando se realizaron los experimentos empleando la mezcla Lys/HSA a pH= 7,9, donde existe la máxima atracción de carga entre las proteínas, se observó un aumento importante en los rendimientos cuánticos de transformación tanto de Lys como de HSA (estos rendimientos se refieren exclusivamente a procesos de entrecruzamiento y no consideran modificaciones oxidativas en la proteína nativa monomérica). Mediante geles de SDS-PAGE se estableció la presencia de una banda importante del dímero covalente HSA-Lys. En menor extensión se observó la presencia de Lys-Lys y, aún en menor cantidad HSA-HSA. Al igual que en los experimentos independientes de las proteínas, el grado de dimerización sensibilizado por RF fue mayor que el observado utilizando MB como sensibilizador. La presencia de dímeros HSA-Lys fue también apreciada cuando la mezcla HSA/Lys fue incubada con AAPH a 37ºC. Los resultados dan cuenta que los procesos fotoinducidos (principalmente por RF) y las reacciones mediadas por radicales libres son capaces de, en condiciones que facilitan la cercanía de las proteínas, inducir el entrecruzamiento covalente de proteínas como Lys y HSA.

Agradecimientos: Este trabajo fue financiado por el Proyecto FONDECYT Nº 1070285 y el Proyecto Puente 05/2009.

P13

PHOTODISSOCIATION OF CHALCOGENIDES: LASER FLASH PHOTOLYSIS AND PRODUCT ANALYSIS STUDY

Juan E. Argüello, Andrea Barrionuevo, Lydia M. Bouchet, Luciana C. Schmidt and Alicia B. Peñéñory

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina, jea@fcq.unc.edu.ar

Key words: Chalcogenides, radicals, laser flash photolysis

The photochemistry of thioetheres has been somewhat sparsely studied over the years; in general, aliphatic thioethers undergo homolytic dissociation, both in solution and in the gas phase. Photohomolysis of aryl thioeters may be followed by in-cage electron transfer to give an ion pair.[1] Selenides and tellurides have been used as a source of ketones by irradiation in the presence of molecular oxygen.[2] However, systematic investigation or basic data such as quantum yields measurement and kinetic information for chalcogenides are scarce at present.

To broaden understanding of the photochemistry of the C-S or C-Se moiety, we present our results on the irradiation of a series of aryl diphenylmethyl sulfides and selenides, such as $ArSCHPh_2$ and $ArSeCHPh_2$. Electron-donating and electron-withdrawing groups were included in the aromatic ring for the sulfides, while for the selenides, phenyl, anisyl and naphthyl derivatives were studied.

The involvement of the intermediates $Ph_2CH^•$, $ArS^•$ and $ArSe^•$ was identified using laser flash photolysis (266 nm, Figure 1). Product analysis (254 nm) gives as a main product 1,1,2,2-tetraphenylethane with the formation of a new carbon-carbon bond and diaryldichacogenides as a main products. All these compounds are formed from the radicals through a coupling reaction. To a lesser extent, H-abstraction products were also observed (eq. 1).

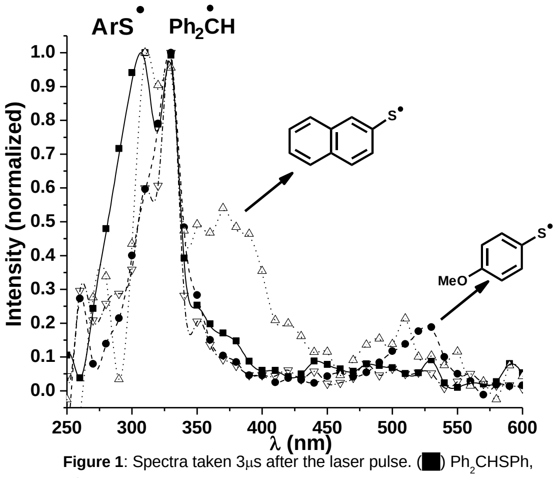
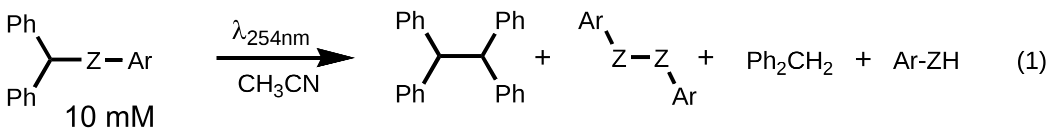


Figure 1: Spectra taken 3μs after the laser pulse. (■) Ph_2CHSPh, (●) $Ph_2CHSC_6H_4OMe$, (△) $Ph_2CHSC_{10}H_7$, (▽) $Ph_2CHSC_5NH_4$



Z = S, Ar = Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-$MeSC_6H_4$, *p*-BrC_6H_4, 2-pyridyl, 2-naphthyl
Z = Se, Ar = Ph, *p*-$MeOC_6H_4$, 1-naphthyl, 2-naphthyl

References

---

[1] (a) Bonesi, S. M.; Fagnoni. M.; Dondi, D.; Albini, A. *Inorg. Chim. Acta* **2007**, *360*, 1230-34. (b) Fleming, S. A.; Jensen, A. W. *J. Org. Chem.* **1993**, *58*, 7135-37.

[2] (a) Hyugano, T.; Liu, S.; Ouchi, A. *J. Org. Chem.* **2008**, *73*, 8861-66. (b) Ouchi, A.; Hyugano, T.; Liu, C. *Org. Lett.* **2009**, *11*, 4870-73.

P14

PHOTOINDUCED GENERATION OF COUMARINE 314 FREE RADICAL

Alexis Aspée[1], Eduardo Pino[1], Emilio Alarcón[2] and J. C. Scaiano[2]
1 Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile.
2 Department of Chemistry, University of Ottawa, Ottawa, Canada.
email: alexis.aspee@usach.cl

Palabras clave: coumarine 314, free radical, antioxidants, rate constant.

The absorbance and fluorescence of coumarine 314 (c314) show a strong bathochromic shift with increasing media polarity which has been attributed to an intramolecular charge transfer excited state. Moreover, this dye has also very high fluorescent quantum yields and long fluorescence lifetimes in a wide range of solvents.[1] In the present report, we studied the formation of c314 free radicals photoinduced by laser irradiation. Time resolved experiments for c314 in cylohexane, using as excitation source a Nd:YAG OPO laser at 430 nm, showed a broad transient absorbance band around 550 nm characteristic of the triplet state. However, experiments carried out in phosphate buffer with 450 nm laser produces a different spectrum with a strong signal ca. 370 nm similar to spectra of phenol derived radicals.[2] The very long lifetime of this transient (ca. 300 μs) not dependent with oxygen concentration also agrees with its identification as a free radical. In addition, this transient was efficiently quenched by different antioxidants such as Tempol, Trolox, cinammic acids (caffeic, ferulic and sinapic acid) and polyphenols (pyrogallol red and quercentin) with high rate constants values ($k = 10^8$-10^9 $M^{-1}s^{-1}$). In particular, after quenching by quercetin it was observed a growing transient 580 nm characteristic of quercetin radicals. The values of the rate constants and their correlation with the oxidation potential of the antioxidants are discussed in terms of electron transfer reaction from the antioxidants towards c314 derived free radical.

Acknowledgments: Financial support from FONDECYT 1085177.

1. Bueno, C., Mikelsons, L., Maretti, L., Scaiano, J. C., Aspée, A. *Photochem. Photobiol.* 2008, **84**, 1535.
2. Brede, O., Orthner, H., Zubarev, V., Hermann, R. *J. Phys. Chem.* 1996, **100**, 7097.

P15

ISOLATION AND PHOTOCHEMICAL PROPERTIES OF THE MAJOR COLORED COMPOUND ARISING FROM GLUCOSE DECOMPOSITION.

Felipe Avila[1], Bertrand Friguet[2] and Eduardo Silva[1]

1 Facultad de Quimica, Pontificia Universidad Catolica de Chile, Santiago 6094411, Chile,
esilva@uc.cl
[2] Laboratoire de Biologie et Biochimie Cellulaire du Vieillissement. UR4 Vieillissement,
Stress et Inflammation. Université Pierre et Marie Curie - Paris 6

Key Words: Oxidative Stress, Glucose Autoxidation, Photosensitization.

The eye lens is a tissue composed mainly by proteins, which has an extremely long lifetime, and for this reason, it is exposed to posttranslational modifications.

These modifications have an accumulative character, leading to alterations in the physical properties, which can alter the correct vision, a disease commonly known as cataract.

Light has been proposed as a risk factor in the cataract generation; however, the reasons for this relationship remain unclear.

Several studies show that the decomposition of glucose and ascorbic acid can contribute to the aggregation of proteins via the Millard reaction; however, the autoxidative pathway of these two molecules has been scarcely studied.

In this work we show that the decomposition of glucose generates a single chromophore that can generate photosensitized reactions.

Glucose (30 mM) was incubated at 37°C in sterile conditions for 10, 20 and 30 days at pH 7.4 and at low oxygen concentration, which is the physiological condition for the eye lens. A gradual generation of a chromophore was observed. This compound presented an absorption maximum at 365 nm and HPLC measurements indicate the presence of a single chomophore. The structure of the compound was elucidated by HPLC-MS and NMR measurements.

The effect of the photosensitized reactions was assayed upon target of biological importance, such as lens proteins and ascorbic acid.

When lens proteins were irradiated with UVA-visible light in the presence of this sensitizer a time dependent photocrosslinking and photo-oxidation were observed, being 0.16 μmol of ascorbic acid decomposed after 60 min of irradiation.

On the other hand, when glucose (30mM) is incubated in the presence of lens proteins (10 mg/mL), in the presence and absence of light, more extensive protein crosslinking is observed in the irradiated system. For the irradiated and non irradiated systems the same amount of free Lys groups was observed, which discards a more extensive glycation in the irradiated system. These data suggest that the chromophore generated by the decomposition of glucose may be produced in the presence of a high amount of lens proteins and could contribute to the deleterious effect of the UVA light in the cataract generation.

Acknowledgments

This work was supported by Proyecto Puente 05/2009. F. Avila gratefully acknowledges CONICYT for a Doctoral and thesis support scholarships.

P16

PHOTOPOLIMERIZATION KINETIC OF SODIUM STYRENESULFONATE ON LAPONITE RD SUSPENSION

Tatiana Batista, Carla C. C. Schmitt y Miguel G. Neumann

Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil
t_batista@iqsc.usp.br

Palabras clave: photopolymerization in situ, clay, composites

In the present work composites of sodium polystyrenesulfonate (PSS) with clay Laponite RD were prepared by *in situ* photopolymerization using Safranine O (SfH^+) as initiator. The photopolymerization kinetics as a function of clay loading (0.5-10 wt%) was study gravimetrically, were the interactions between monomer, clay and dye were studied by UV vis., fluorescence and flash photolysis, aiming to understand the role of clay morphology on the reaction kinetics. Emission spectra of StyS (sodium styrenesulfonate) aqueous solutions at low (0.01 M) concentration present only one peak at 307 nm, due to the monomol emission. By increasing the concentration, the emission intensity decreases and the maximum is shifted to the red. At concentrations above 0.1 M a new peak assigned to the aggregate emission grows-in at 410 nm, with no effect of the amount of clay. It suggests that presence of the clay have no effect in the hydrotropic aggregation of the monomers. The addition of StyS to the aqueous solution of SfH^+ induces an initial aggregation mainly due to the electrostatic interaction between the negatively charged monomers and the cationic dye, giving rise to the aggregation peak at lower wavelengths as observed by UV vis. At higher concentrations, the absorption intensity increases and the maximum starts shifting to the red. This behaviour is attributed to the dye disaggregation that is due to the redistribution of the dye molecules between monomer aggregates. However, when StyS is added to a dye solution containing Laponite in suspension the absorption maximum does not shift, suggesting that the interaction between the clay surface and the dye molecules prevails over the dye-StyS interactions. The presence of clay allows a better disaggregation of the initiator molecules, decreasing the quenching of the excited states that lead to the radicals that initiate polymerization. Increasing the loading of clay in the polymerization mixture promotes higher and faster polymerization conversions. Irradiation of the reaction mixture for 21 h in the absence of clay resulted in a conversion of 11%. When 20% of clay was added, the conversion increases by 39% for the same irradiation time. Data of flash photolysis indicated that the presence of clay promotes an increase in the lifetime of the protoned species of Safranine, which is responsible for the photopolimerization initiation.

The authors thank FAPESP and CAPES for financial support.

P17

ESTUDO FOTOFÍSICO DE TIOXANTONAS ANELADAS ATRAVÉS DE FOTÓLISE POR PULSO DE LASER

Douglas Rosa Bernardo[*], **Miguel Guillermo Neumann**[*], **Carla Cristina Schmitt Cavalheiro**[*]

[*] Departamento de Físico-Química, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil, Av Trabalhador São Carlense, 400, CP 780, CEP 13560-350, Tel + (55)-(16)-33739935, douglasrosa@hotmail.com

Palavras chave: Tioxantonas, Fotoiniciadores, Fotólise por pulso de laser

Tioxantonas são compostos com estrutura de uma cetona aromática que apresentam as características de um corante. Esses compostos são utilizados como fotoiniciadores em reações de polimerização radicalar fotoiniciadas. Fotoiniciadores podem atuar na polimerização através de dois mecanismos, tipo I ou II sendo que a tioxantona promove a reação através de um mecanismo tipo I. Já na polimerização fotoiniciada por tioxantonas aneladas, a formação dos radicais ocorrem na presença de oxigênio devido a estabilização através do grupo anelar. Desta forma, espera-se que as tioxantonas aneladas participem da reação de polimerização através de um mecanismo do tipo II.

A Figura 1 ilustra as estruturas químicas estudadas neste trabalho.

(A) **(B)**

Figura 1. Estruturas químicas dos compostos (A) *5-thia-naphthacene-12-one*, (TX-Np); e (B) *5-thia-pentacene-14-one*, (TX-A) .

Para verificar o comportamento fotofísico desses compostos foram realizados estudos de absorção UV-Vis e Fotólise por pulso de laser em três solventes hidroxílicos: metanol, 1-propanol e 1-hexanol. Esses estudos mostraram que a absorção na região do visível não é afetada significativamente pela viscosidade do solvente, pois não se observou alteração da região de absorção. Os estudos de fotólise por Pulso de Laser foram realizados para investigar os transientes formados por esses compostos nos diferentes solventes, em atmosfera de N_2 e em ar. Os espectros demostraram a existência de duas regiões de absorção para a TX-A em 410 e 510 nm, já o composto TX-Np apresentou absorção em 340, 430 e 590 nm. Os tempos de vida das espécies formadas foram obtidos através do tratamento matemático das curvas de decaimento. Verificou-se um aumento dos tempos de vida dos transientes com o aumento da polaridade do solvente. Os estudos realizados em ar atmosférico da TX-A em 410 nm apresentaram tempos de vida de 0.22; 0.25 e 0.38 ns em metanol, 1-propanol e 1-hexanol respectivamente e da TX-Np em 350 nm 0.30; 0.41 e 0.63 ns. Em atmosfera de N_2, os decaimentos revelaram a presença de dois tempos de vida na escala de microssegundos.

Agradecimentos: FAPESP e CNPq.

P18

DETERMINATION OF COMPOSITION OF DISSOLVED ORGANIC MATTER OF VOSSOROCA LAKE BY FLUORESCENCE SPECTROSCOPY

Daniele Botelho, Karina Scurupa Machado, Sandro Froehner

Department of Environmental Engineering, Federal University of Parana, Curitiba-PR, Brazil, 81531-980, froehner@ufpr.br

Keywords: dissolved organic matter, fluorescente spectroscopy, water resources

Dissolved organic matter (DOM) are heterogeneous mixtures of a variety of organic compounds, consisting of aromatic, aliphatic, phenolic, and quinolic functional groups with varying molecular sizes and properties (Aiken et al., 1985). DOM is known to play important roles in the interaction and transport of many toxic organic and inorganic compounds and nutrient cycling throughout the environment (Choppin, 1992; Chen et al., 2003). Fluorescence of DOM accounts for a significant portion of the fluorescence in both natural fresh water and oceanic water samples. Here, we used fluorescence spectroscopy to get information about the source and main composition of organic matter present in water.

The samples were collected in Vossoroca lake located in Curitiba-Brazil. All water samples were filtered using a 0.45 μm membrane (cellulose nitrate) to remove undissolved particulate materials. All fluorescence spectra were recorded on a F-4500 Hitachi Spectrophotometer. The excitation wavelength ranged was from 290 to 480 nm, and the emission wavelength ranged from 400 to 600 nm.

The synchronous fluorescence spectra had shown that there was a presence of phenolic groups, aminoacids with aliphatic groups in the molecule. Recently, the fluorescence index use was proposed to distinguish microbially from terrestrially organic matter. The index is defined as the ratio of fluorescence emission intensity at 450 nm to 500 nm (E_{450}/E_{500}). The microbially derived organic matters has index approximately 1.9, while terrestrially organic matter show a fluorescence index approximately 1.4. Here we found values of E_{450}/E_{500} close to 1.4, indicating that the origin of organic matter is from terrestrially source. Fluorescence peak positioning and shift, peak intensity, and peak broadening appear to be the most useful observations, and could be correlated to such structural signatures as molecular sizes and contents of aromatics, phenolics, carboxyl and hydroxyl functional groups.

Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P. (1985) Humic substances in soil, sediment, and water. John Wiley Sons.

Choppin, G. R. (1992) The rol of natural organics in radionuclide migration in natural aquifer systems. Radiochim. Acta 58(9), 113-120.

Chen, J., LeBoeuf, E. J., Dai, S., Gu, B. (2003) Fluorescence spectroscopic studies of natural organic matter fractions. Chemosphere 50(2), 639-647.

Acklnowledgements: Funding for this research was supported by CNPq (Grant 577060/2008-2).

P19

orto-ARILACIÓN DE *N*-(*orto*-HALOBENCIL)ARILAMIDAS MEDIANTE PROCESOS DE TRANSFERENCIA ELECTRONICA FOTOINDUCIDA. ESTUDIO TEÓRICO COMPUTACIONAL

María E. Budén, **Viviana B. Dorn, Roberto A. Rossi y Adriana B. Pierini**

INFIQC, Dpto. de Química Orgánica, Facultad de Cs. Químicas, Universidad Nacional de
Córdoba, (5000) Córdoba, Argentina, Medina Allende y Haya de La Torre, Ciudad
Universitaria,
E-mail: adriana@fcq.unc.edu.ar

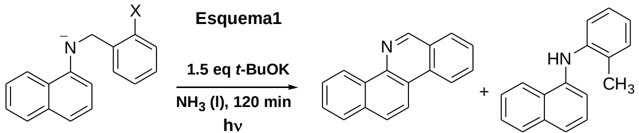
Palabras clave: Transferencia de Electrón – Estudio Computacional – TD DFT

El mecanismo $S_{RN}1$[1] es un proceso en cadena que involucra radicales y radicales aniones como intermediarios, iniciándose generalmente, mediante una transferencia electrónica fotoinducida (TEF) desde el nucleófilo al sustrato. Se forma así un radical anión que por posterior eliminación del grupo saliente genera las especies radicalarias que propagan el ciclo.

En este sentido, los aniones de N-(*o*-halobencil)arilaminas son sustratos que poseen en la misma estructura tanto el grupo saliente (X = I, Cl, Br) como el centro nucleofílico (R_2N^-). De esta forma se pueden obtener fenantridinas (*C*-ciclación) a través de una reacción de acople intramolecular mediada por TEF.

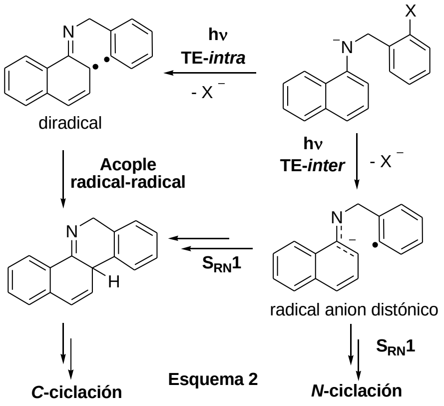
En un estudio experimental realizado en NH_3(liq.) con diferentes aniones de N-(*o*-halobencil) 1-naftilaminas y bajo fotoestimulación, se observó una variación de la distribución de productos de ciclación en función del grupo saliente (Ver Esquema 1). Con el objeto de evaluar el mecanismo implicado y poder explicar los factores electrónicos y geométricos responsables de los resultados experimentales obtenidos, se realizaron reacciones bajo diferentes condiciones de trabajo, conjuntamente con un estudio computacional aplicando el funcional B3LYP y las bases LANL2DZ, 6-31+G* y 6-31G*.

Esquema1



1 eq ($1x10^{-3}$ M)	*C*-ciclación	*N*-ciclación
X=Cl	53%	41%
X=Br	55%	34%
X=I	86%	8%

A partir de los resultados obtenidos podemos proponer que la diferencia observada experimentalmente, respondería a la vigencia de dos mecanismos de TEF que competirían en la formación del producto de *C*-ciclación (Ver Esquema 2). Para evaluar la TEF intramolecular se realizaron los correspondientes cálculos de TD-DFT para cada anión. En principio, la naturaleza del grupo X sería la responsable de favorecer un mecanismo u otro, permitiendo al sustrato dar acople radical-radical o radical-anión mediante una reacción fotoquímica.



Esquema 2

---

[1] Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. *Chem. Rev.* **2003**, *103*, 71−167.

P20

ASOCIACIÓN DE CALCEÍNA A ALBÚMINA DE SUERO HUMANA. UNA COMPARACIÓN DE MÉTODOS ESPECTROSCÓPICOS, CALORIMÉTRICOS Y DE SEPARACIÓN FÍSICA.

Calderón C[1]., Abuín E.[1], Lissi E.[1], Watson Lho[2]

(1) Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile. (2) Universidade de Campinas, Brasil
E-mail: c_calderon13@yahoo.com

La asociación de colorantes a albúmina de suero humana (HSA) ha sido ampliamente estudiada [1,2] por distintos métodos; sin embargo muy pocos estudios han sido realizados comparando los resultados obtenidos por distintas técnicas. En el presente trabajo, se presentan un estudio de la asociación de calceína a HSA evaluada a partir de medidas espectroscópicas (efecto de HSA en el espectro de absorción y fluorescencia del colorante), estudios calorimétricos (titulación calorimétrica isotérmica) y de separación física (microcentrifugación). Los resultados obtenidos por las distintas técnicas son compatibles con un modelo de asociación a sitios, permitiendo evaluar la constante de asociación para el proceso de unión obteniéndose valores similares por las distintas técnicas.

Los autores agradecen a Fondecyt (Proyectos 1095036 y 1070285) el financiamiento otorgado para la realización de este trabajo. C. Calderón agradece a Conicyt por un beca de doctorado

1- Alarcon, A., Edwards, A. M., Aspée, A., Morán, F. E., Borsarelli, C., Lissi, E., Gonzalez-Nilo, D., Poblete, H., Scaiano, J. C. Photochem. Photobiol. Sci. 2010, 9, 93-102.
2- Qin, C., Xie, M. X., Liu, Y., Biomacromolecules, 2007, 8, 2182-2189

P21

FENTON PROCESS IN THE DEGRADATION OF THE CRUDE OIL AROMATIC FRACTION IN NATURAL SAND

Fábio Cal Sabino, Luciana Natália Cividatti, Flávia Corrêa Zanuto, Eduardo Di Mauro and Carmen Luisa Barbosa Guedes*

Laboratório de Fluorescência e Ressonância Paramagnética Eletrônica (LAFLURPE), CCE,
Universidade Estadual de Londrina, Londrina, Brasil, *e-mail:* *****carmen@uel.br

Keyword: photo-Fenton, fluorescence, salinity.

The main objective of this study was to evaluate the photo-Fenton process, occurring in media of high salt concentration, acting in the degradation of aromatic fraction of oil trapped in natural sand. In the case of a multi component mixture, the technique used for analysis was synchronous fluorescence spectroscopy, in addition measures pH, intensity of solar radiation and temperature of samples during treatment. Mean values of physicochemical parameters monitored during treatment of sand contaminated with oil it were the pH around 5; average temperature in samples of about 30°C and intensity of sunlight in the period was around 200 W/m^2. By the integrated area of fluorescence, we observed that treatment involving sunlight without addition of peroxide in saline medium reduced by 27% the intensity of fluorescence of aromatics. Considering the treatment with the addition of oxidizing agent in saline, without radiation, the fluorescence was reduced by 44%. However, the action of sunlight in synergy with the peroxide on the contaminants caused a decrease of fluorescence corresponding to the degradation of aromatic fraction of oil in the sand in about 70%. Solar radiation involved in photo-Fenton process contributed to adjustment and control of pH in more acidic conditions less favorable to Fenton process (no light). The addition of 0.8 M or 0.08 M ferrous sulphate in saline middle, serving as a natural increase of iron in the sand, resulted in an increased 79% and 63% for the degradation of aromatic compounds in oil, whereas the iron endogenous, in the approximate concentration of 1.53 ppm (0.003M) was sufficient to decrease the fluorescence by 68%. Regarding the integrated area of fluorescence spectra, reduced 67% when the photo-Fenton process occurred in saline with added 0.8 M iron sulphate. When the treatment of contaminated sand occurred in the presence of endogenous iron, the degradation of aromatic crude oil it was so slight, reducing only 29% of the area of fluorescence. It was concluded that the photo-Fenton treatment could be used in the remediation of environments impacted by oil spill, conducted with low concentrations of iron ions, preferably natural iron, because the high acidity of the medium is likely to impact further environment. In the case of aquatic environments with high concentrations of dissolved salts, ferrous sulfate could be added, but always carefully to use the lowest concentration of reagents seeking better efficiency, lower cost and mitigation of environmental impact.

Acknowledgments: CAPES, CNPq e Fundação Araucária.

P22

ESTUDOS FOTOQUÍMICOS E FOTOFÍSICOS DO COMPLEXO *cis*-$[Ru(phen)_2(amq)_2]^{2+}$

Canesqui P. L. e **Carlos M. R.**

Departamento de Química, Universidade Federal de São Carlos, São Carlos - Brasil
leticia_priori@yahoo.com.br

Palavras chave: Fotoquímica, Rutênio, Alzheimer

Aminoquinolinas são moléculas luminescentes que apresentam potencial aplicação no sistema neurológico. A coordenação destas moléculas a complexos polipiridinicos de Ru(II) podem aumentar a biodisponibilidade destas moléculas no meio fisiológico. Também a liberação destas moléculas pela técnica fotoquímica pode tornar estes complexos potenciais candidatos a sistemas de entrega seletiva e controlada destas moléculas no meio fisiológico de forma que possam ser administrados a doses menores, diminuindo assim a toxicidade e aumentando sua biodistribuição. As propriedades luminescentes desses compostos possibilitam sua aplicação como sondas biológicas permitindo o mapeando do local de entrega da molécula e permitindo assim a atuação como diagnóstico. Neste trabalho pretendemos sintetizar, caracterizar e avaliar as propriedades fotoquímicas e fotofísicas de uma série de complexos polipiridnicos de Ru(II) coordenados a aminoquinolinas do tipo cis-$[Ru(phen)_2(Amq)_2]^{2+}$ (complexo **1**). Complexo 1 foi preparado pela substituição de dois ligantes cloreto em cis-$Ru(phen)_2Cl_2$ pela Amq sob refluxo e agitação constante em solução água/etanol. Este complexo apresenta solubilidade em água (soluções tampão: fosfato, pH 7,02; KCl/HCl pH 2,21), absorção intensa no visível (λ_{max} = 476 nm, ε_{max} = 10000 $mol^{-1}.L.cm^{-1}$) atribuídas a bandas de MLCT (Ru → phen/amq) pela comparação com sistemas homólogos e por cálculos de OM usando a teoria funcional da densidade dependente do tempo (TDDFT), e luminescência intensa a 412 nm atribuída ao ligante amq. A irradiação do complexo $[Ru(3amq)_2(phen)_2]^{2+}$ com luz de 420 nm levou a liberação da amq que foi confirmada por técnicas espectroscópicas (UV-vis, ^1H RMN) e eletroquímicas (voltametria cíclica). A liberação fotoquímica da amq também foi acompanhada por técnicas de luminescência no estado estacionário. Nestes experimentos a irradiação do complexo com luz de 420 nm em meio aquoso (pH 7,4 tampão fosfato) levou a um aumento significativo na intensidade relativa das emissões a 412 nm coerente com a presença da amq livre (λ_{max} = 412 nm). Os resultados obtidos até o momento são importantes para a entrega seletiva e controlada da Amq no meio fisiológico.

P23

TIOLES QUIMISORBIDOS SOBRE PARTICULAS DE SILICE. GENERACION Y COMPORTAMIENTO DE ESPECIES REACTIVAS DEL AZUFRE

Paula Caregnato*, Malcolm D.E. Forbes#, Daniel O. Mártire* y
Mónica 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,dmartire@inifta.unlp.edu.ar, gonzalez@inifta.unlp.edu.ar

Caudill Laboratories. Department of Chemistry, CB #3290. University of North Carolina Chapel Hill, NC 27517, USA. mdef@unc.edu

Palabras clave: Flash Fotolisis, Radicales Tiilo, Silanizacion.

Los tioles son un grupo de sustancias extraordinariamente eficientes como antioxidantes. Los biotioles protegen a las células contra las consecuencias de los daños inducidos por radicales libres. Los seres vivos están continuamente expuestos en el medio ambiente a numerosos compuestos que contienen tioles y los disulfuros derivados, como por ejemplo los tioles presentes en alimentos como el ajo y ciertos pescados.

Sin embargo, por oxidación de los tioles a nivel celular, se forman especies del azufre que a su vez pueden oxidar y posteriormente inhibir la actividad de ciertas proteínas y enzimas.

Estas especies químicas son conocidas como especies reactivas del azufre (Reactive Sulfur Species, RSS) e incluyen radicales centrados en el azufre, disulfuros, disulfuros S-óxidos y ácidos sulfínicos y sulfónicos [1,2].

El estudio de las reacciones de los tioles en medios restringidos, como inmovilizados sobre superficies de sílice, podría resultar una aproximación interesante al estudio de la reactividad y comportamiento de los RSS en medios controlados.

En este trabajo se derivatizaron partículas de sílice (gel de sílice y sílice pirógena) con 3-mercaptopropiltrimetoxisilano (MPTS) [3] generándose la sílice modificada (Sil-SH) con el objetivo de utilizar la matriz de sílice como soporte para estudiar la capacidad antioxidante de los tioles.

Las RSS fueron generadas a partir de los tioles quimisorbidos por reacción con agentes oxidantes como el radical sulfato, generado por fotolisis de soluciones acuosas de $Na_2S_2O_8$.

Se realizaron experimentos de láser flash fotólisis (λ_{exc} 266 nm) y se obtuvieron los espectros de absorción de las RSS formadas a partir del radical sulfato.

[1] Giles, G.I.; Jacob, C., Biol. Chem. 383 (2002) 375-388.
[2] L. Wlodek, Pol. J. Pharmacol. 54 (2002) 215-223.
[3] Arakaki, et al. J. Environ. Monit., 5 (2003) 366–370.

P24

ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF LANTHANIDE LACUNARY LINDQVIST TYPE HETEROPOLYOXOMETALATES FAMILY

Desmond Mac-Leod Carey[*], Alvaro Muñoz-Castro*, Luis Alvarez-Thon[$],
Ricardo Veloso*, Carlos Bustos[§] and Ramiro Arratia-Pérez[*]

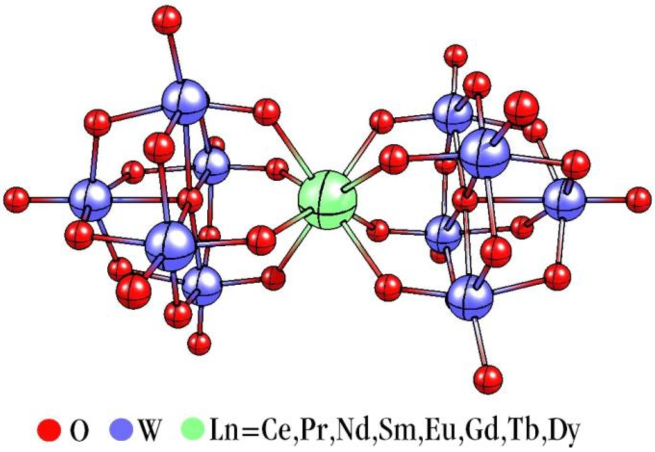
*Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales, Universidad Andres Bello, República 275, Santiago, Chile, *dessitouc@gmail.com*

[$]Departamento de Ciencias Físicas, Facultad de Ingeniería, ,Universidad Andres Bello, República 275, Santiago, Chile. *quaternionic@gmail.com*

[§]Instituto de Química, Facultad de Ciencias,Universidad Austral de Chile, Los Laureles s/n, Campus Isla Teja, Valdivia, Chile. *cbustos@gmail.com*

Palabras clave: Polyoxometalates, Heavy Metal, Lanthanide, DFT.

The photochemistry of polyoxometalates (POMs) is very well known. More than 90 years ago, it was found that the α-Keggin tungstate $H_3[PW_{12}O_{40}]$ was reduced photochemically to yield a blue-colored species which was reoxidized by air and other oxidizing agents[1]. These so-called "heteropoly blues" have been used for colorimetric analysis of P, Si, As, and Ge elements and for the determination of uric acid, sugar and other biological compounds[2].



Since the metal ions in the oxidized POMs have d^0 electronic configurations, the only absorption band which occurs is due to the oxygen-to-metal (O→M) ligand-to-metal charge transfer (LMCT). On the other hand, POMs containing heteroatoms or different metal ions (hetero-POMs) can modify and/or enhance these O→M LMCT[3].

In this work we describe the electronic structure, spin-orbit effects over the bonding structure and the photoluminescent behaviour of a complete serie of Lanthanide lacunary Lindqvist-type hetero-POMs[4], see figure, $[Ln\{W_5O_{18}\}_2]^{-9}$ with Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, based on DFT and TD-DFT calculations including Relativistic Scalar and Spin-Orbit corrections within a four-fold symmetry group.

References

1. Rindel, M. S. *African J. Sci*. **1916**, *11*, 362.
2. a) Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*; Wiley and Sons: New York, 1966. b) Wu, H. *J. Biol. Chem*. **1920**, *43*, 189
3. Yamase, T.; Sugeta, M. *J. Chem. Soc., Dalton Trans*. **1993**, 759
4. T. Ozeki, T. Yamase, *Acta Cryst.* **1994.** *B50*, 128-134

Acknowledgements

The authors thank the financial support of: FONDECYT Grant 1070345, UNAB Grants UNAB-DI-02-09/R, UNAB-DI-02-08/R, UNAB-DI-09-09/I, UNAB-DI-06-09/I; PROJECT MILLENNIUM Grant No. P07-006–F; and the Fellowship Beca Doctoral UNAB.

P25

EFFECT OF MICELLE-LIKE AGGREGATES OF HUMIC ACIDS ON SINGLET OXYGEN EXPERIMENTS

Luciano Carlos[*], Brian Wett[#], Mónica C. Gonzalez[*], Peter Ogilby[#] and Daniel Martire[*]

[*] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CCT-La Plata-CONICET, Universidad Nacional de La Plata, La Plata, Argentina.
e-mail: lcarlos@quimica.unlp.edu.ar
[#] Center for Oxygen Microscopy and Imaging (COMI), Departement of Chemistry, University of Aarhus, Aarhus, Denmark.

Keywords: singlet oxygen, humic substances, aggregates

Humic acid (HA) form micelle-like aggregates in solution with a hydrophobic interior and hydrophilic periphery. In soil environments, such aggregates can play important roles in the transport, bioavailability and biodegradability of hydrophobic organic pollutants. On the other hand, photolysis of HA leads to the formation of a complex mixture of reactive species. Among these species, singlet oxygen [O_2 ($^1\Delta_g$)] is argued to be responsible for the degradation of many organic pollutants.

In this work, the effect of the formation of HA aggregates on the O_2 ($^1\Delta_g$) lifetime was ivestigated. Additional assays were carried out in the presence of hydrophylic (TMPyP) and hydrophobic (TPP) porphyrins as the sensitizers, and rubrene and NaN_3 as the O_2 ($^1\Delta_g$) quenchers. Also, the shape and the size of the HA aggregates and sensitizers location in the aggregates were analyzed by microscope techniques.

All the HA dispersions were made in D_2O and the pH range 8.5-10.5. The singlet oxygen phosphorescence at 1270 nm was detected both in cuvette and in microscope experiments. In the latter case, the laser beam was focused either on the micelle-like aggregates or on the bulk phase.

The results showed the formation of micelle-like aggregates above the critical micelle concentration (cmc = 0.4 g L^{-1}, as determined by using the fluorescence probe pyrene). These aggregates have no uniform size (0.5 - 30 μm average diameter). In the presence of both TMPyP and TPP, microscope images showed that TMPyP is located in the exterior surface of the aggregates, whereas TPP is mainly inside the aggregates.

Quenching of O_2 ($^1\Delta_g$) experiments performed in the cuvette showed an increase of $1/t_\Delta$ with increasing [HA] in the range 0.05-1.6 g L^{-1}. The plot shows two linear regions. The intersecetion of the two slopes of the straight lines corresponds to a HA concentration close to the cmc. The same behavior was obtained when TMPyP or TPP were added to the HA dispersion. Addition of NaN_3 (1.0 mM) lead to complete quenching of the O_2 ($^1\Delta_g$) at all HA concentrations tested.

Microscope experiments showed that only when TMPyP was used as the sensitizer and the laser beam was focused on the aggregates, singlet oxygen was detected (t_Δ = 13.6 μs).

The environmental consequences of these results are discussed.

P26

INTERACCION ENTRE GLICLAZIDA Y ALBUMINA DE SUERO HUMANO

Cecilia Challier, Susana Criado y M. Alicia Biasutti

Departamento de Química, Facultad de Ciencias Exactas, Fco. Qcas. y Naturales
Universidad Nacional de Río Cuarto, Río Cuarto, Argentina, Dirección, e-mail:abiasutti@exa.unrc.edu.ar

Palabras clave: asociación, gliclazida, HSA,

Las sulfonilureas han sido prescriptas, desde los años 50, como agentes hipoglucémicos. Los mismos pertenecen a la clase de antidiabéticos orales conocidos como sulfonilureas. Dichos antidiabéticos son indicados en el tratamiento de la diabetes *mellitus* tipo 2 y actúan aumentando la liberación de insulina de las células *Beta* del páncreas.[i], [ii] Actualmente, los más utilizados son los medicamentos de segunda generación, que contienen como principios activos glicazida, glimeperida, glipizida o glibenclamida[ii]. Por otro lado en la sangre el transporte de diversos compuestos y drogas (ácidos grasos, hormonas, bilirrubina, medicamentos, etc.)[iii], [iv,v] se realiza a través de la albúmina de suero humano (HSA). En tal sentido, se considera de relevancia investigar la interacción entre la proteína y el sustrato de interés: gliclazida (Gli) y la posible susceptibilidad a la fotodegradación del antidiabético libre y unido a HSA. Dicha interacción fue investigada utilizando espectroscopia UV-Visible y de fluorescencia. Los resultados experimentales mostraron que el “quenching” de fluorescencia de Gli por HSA resulta de la formación de un complejo Gli-HSA en el estado fundamental; el quenching estático fue confirmado por determinaciones de tiempos de vida y efecto de la temperatura. Asimismo, los parámetros de “binding”, K_A y n, fueron calculados a partir de los resultados de quenching de fluorescencia a 11,5 ºC, 17 ºC y 37ºC resultado los siguientes valores de K_A: 2188, 2344 y 2951 l/mol, respectivamente. Se estimaron los parámetros termodinamicos ΔH^o, ΔS^o y ΔG^o a partir de la ecuación de van´t Hoff, resultando valores positivos de ΔH y ΔS, lo cual indica que las interacciones entre HSA y Gli son predominantemente de carácter hidrofóbico. La distancia R (parámetro de Förster) entre el donor HSA y el aceptor Gli fue obtenido de acuerdo a un tratamiento de transferencia de energía por resonancia.

Por otro lado, se esta estudiando la fotodegradación de Gli libre y posteriormente asociada a HSA.

---

[i]**.** Sawada F, Inoguchi T, Tsubouchi H. ,Sasaki S., Fujii M., Maeda Y., Morinaga H. Nomura M., Kobayashi K. Takayanagi R. **(2008)** *Metabolilsm Clinical and Experimental 57, 1038-1045.*

[ii] Remko M. **(2009)** *J. Molecular structure: THEOCHEM 897, 73-82.*

[iii] Wang Yan-qing, Tang Bo-ping, Zhang Hong-nmei, Zhou Qiu-hua, Zhang Gen-cheng **(2009)** *J. Photochem. Photobiol. B: Biology* 94, 183-190.

[iv] Honore, B. **(1990)**, *Pharmacol. Toxicol*. 66,7.

[v] Mallick A., Purkayastha, P., Chattopadhyay **(2007**) *J. Photochem. Photobiol. C:Photochemistry Reviews* 8, 109-127.

P27

SÍNTESE, ESTUDOS FOTOQUÍMICOS E DE INIBIÇÃO ENZIMÁTICA DO COMPLEXO *CIS*-$[RU(PHEN)_2(APY)_2]^{2+}$ VISANDO A TERAPIA FOTODINÂMICA NO TRATAMENTO DO MAL DE ALZHEIMER

Guilherme Luiz Chinini[*] **e Rose Maria Carlos**[#]

* Departamento de Química, Universidade Federal de São Carlos, São Carlos, Brasil,
e-mail: guilhermechinini@dqufscar.com.br
\# Departamento de Química, Universidade Federal de São Carlos, São Carlos Brasil,
e-mail: rosem@ufscar.br

Palavras Chave: Complexos de Rutênio, Fotoquímica, Hipótese Colinérgica.

A descoberta que aminopiridinas (Apy) desempenham funções importantes no sistema nervoso central (SNC), atuando como bloqueadores de canais de íons K^+ e em várias doenças neurodegenerativas, têm estimulado o interesse na química e bioquímica da Apy. Imobilizar este ligante a um complexo de metal de transição tem como principal alvo construir um sistema de fármaco mais seletivo, menos tóxico e mais eficiente aliado a terapia fotodinâmica. Com esses objetivos este trabalho apresenta a síntese e caracterização do complexo *cis*-$[Ru(phen)_2(Apy)_2]^{2+}$ assim como o estudo fotoquímico e de inibição da enzima da enzima Acetil Colinaesterase com base na hipótese colinérgica.

Efetuou-se a síntese do complexo em 4 etapas, partindo do $RuCl_3.3H_2O$. O produto final *cis*-$[Ru(phen)_2(Apy)_2](PF_6)_2$ foi caracterizado por RMN de ^1H, (8-9 ppm$_{phen}$ 3-4ppm$_{NH2}$), Voltametria Cíclica ($E_{1/2(RuIII/II)}$ = 1200 mV) e de Pulso, Espectroscopia UV-Vis (banda intensa MLCT em 450 nm (10000)em acetonitrila), Absorção no Infravermelho ($\upsilon = 3600\ s^{-1}NH_{2est}\ \upsilon = 318\ s^{-1}RuN_{est}$,).

Os estudos fotoquímicos foram realizados com luz contínua (420 nm) e acompanhados pelas técnicas espectroscópicas UV-Vis e Voltametria Cíclica em acetonitrila e tampão Tris/HCl pH=8,0. A atividade fotoquímica foi observada pela formação de dois diferentes complexos a medida que o ligante Apy era liberado em solução, *cis*-$[Ru(phen)_2(S)(Apy)]^{2+}$ e *cis*-$[Ru(phen)_2(S)_2]^{2+}$ (S = acetonitrila ou água).

Os estudos de inibição enzimática foram efetuados com base no método colorimétrico adaptado de Ellman 1963, onde avaliou-se a potencialidade como inibidor do complexo frente a enzima Acetil Colinaesterase assim como para o ligante 4Apy livre e o princípio ativo de referência Tacrina®. O complexo também teve sua atividade de inibição enzimática avaliada com a ação fotoquímica, assim como o estudo da forma de inibição e da influência do tempo de incubação. Os resultados obtidos mostram que a taxa de reação sem ação de qualquer inibidor foi de 22,50 µmol L^{-1} min^{-1}, e para a adição de 3,7 µM de inibidor determinou-se 8,56 µmol L^{-1} min^{-1} para o complexo, 20,56 µmol L^{-1} min^{-1} para o ligante Apy livre e 0,27 µmol L^{-1} min^{-1} para o inibidor de referência Tacrina®. Não obsevou-se variação na taxa de reação no uso de diferentes tempos de incubação, 0, 10 e 60 min para o sistema complexo e enzima.

O complexo estudado tem-se mostrado um eficiente sistema de fármacos inteligentes, uma vez que tem apresentado boa sensibilidade frente à fotólise contínua, além do auxilio no sistema de ação baseado na hipótese colinérgica.

P28

RUBIADINA: FOTOSENSIBILIZANTE NATURAL Y SU POTENCIAL APLICACIÓN EN TERAPIA FOTODINAMICA.

Comini Laura[1], Fernandez Ivana[2], Nuñez Montoya Susana[1], Cabrera José[1] y Rivarola Viviana[2]. [1] Fcognosia, FCQ-UNC IMBIV-CONICET. Cba., Arg.
[2] Dpto. Biol. Mol. Fac. Cs. Exs. FQca y Nat. UNRC. Río IV, Arg.
E-mail: lcomini@fcq.unc.edu.ar

Palabras claves: Rubiadina, *Heterophyllaea pustulata*, Terapia Fotodinámica.

La Terapia Fotodinámica (TFD) se basa en la toxicidad inducida en el tejido tumoral por acción combinada de un fotosensibilizante (FS) y luz. Rubiadina (**1**); antraquinona (AQ) aislada de *Heterophyllaea pustulata* es un FS cuyas propiedades fotoquímicas y actividad fotodinámica *in vitro* fueron estudiadas previamente, con resultados que permiten considerarla como un buen candidato para la TFD *in vivo*. En este trabajo se evalúa la potencial aplicación de **1** en TFD, utilizando en el diseño experimental un modelo de tumor animal. Para ello ratones hembras Balb/c (20-22 g) portadores de tumores (implante subcutáneo de la línea celular LM-2: $1x10^6$ células/ml contenida en 0,1 ml de buffer fosfato estéril), con un diámetro externo de 5-6 mm fueron separados en cuatro grupos, recibiendo cada uno de ellos, diferentes tratamientos. *Grupo A*: animales con tumor que recibieron una administración intraperitoneal (IP) de **1** (80 mg/Kg, dosis no tóxica)[1] e irradiación de los tumores a las 24 y 48 hs post-inyección, correspondiente al tiempo de acumulación y permanencia del compuesto en el tumor[1]. Para ello el área que contenía el tumor fue iluminada por una lámpara actínica (TL 20 W / 03, Philips), que emite en la región del UV-Visible (380-480 nm) con un máximo de emisión a 420 nm, a razón de 2 J/cm^2 (50 minutos) por cada sesión. *Grupo B:* animales con tumor que recibieron inyección IP de **1** y fueron mantenidos en oscuridad. *Grupo C:* animales con tumor que sólo recibieron iluminación. *Grupo D*: animales con tumor que no recibieron ningún tratamiento. La regresión del tumor fue analizada mediante la medición del mismo en tres dimensiones usando calibre y en base a la siguiente ecuación: $V = L x W x H x 0.5636$ según literatura[2], donde V es el volumen del tumor, L, W y H se refiere a la longitud, ancho y altura del mismo respectivamente. La medición del tumor fue llevada a cabo durante 10 días luego del tratamiento. Los resultados demostraron que los tumores de los animales de los grupos B, C y D incrementaron su tamaño en el período de observación y la diferencia entre los tres grupos no fue estadísticamente significativa. En contraste, un 84% de los animales del Grupo A mostró resultados alentadores. El 50% presentó regresión total del tumor más allá del período de observación. El 34% no sufrió modificaciones respecto al tamaño inicial del tumor y solamente en un 16% el tumor se desarrolló de manera similar a los controles. Los resultados preliminares anteriormente expuestos, señalan a **1** como un promisorio FS natural para su aplicación en TFD y sobre el cual, se continuarán profundizando los estudios para determinar su potencialidad terapéutica.

Bibliografía:
1) Comini L, Fernandez I, Nuñez S, Cabrera J y Rivarola V. Biodistribution and Acute Toxicity Evaluation in vivo of the Natural Anthraquinones**.** BIOCELL (2009).
2) Alvarez, M.; Príncipe, F.; Romanini, C.; Bergesse, J.; Bertuzzi, M.; Romanini, C.; Durantini, E. and Rivarola, V. (2004): Photodiagnosis and Photodynamic Therapy, 1, 335-344.

P29

INFLUENCE OF LIPIDS DOMAINS IN THE VESICLE-VESICLE FUSION PROCESS.

Francisco Javier Cuevas[*], **Andrés Eliu Arce**[&], **Carlos Patricio Sotomayor**[#] **and Luis Felipe Aguilar**[#]

[*] Departamento de Ciencias Básicas, Universidad Santo Tomás, Av. Limonares 190,
Viña del Mar, fcuevasc@santotomas.cl
[&] Ingeniería en Biotecnología, Escuela de Ingeniería, Universidad Viña del Mar, Viña del Mar,
Chile, Agua Santa 7055.
[#] Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso,
Valparaíso, Chile, Av. Universidad 330, Curauma. laguilar@ucv.cl; psotomay@ucv.cl

Keywords: vesicles fusion, micro domains, lipids.

In the last years a lot of studies about the "phenomena" of fusion vesicle has been developed, to understand the intra cell transport phenomena, exocytosis and specially to optimize the fusion process of vesicles used as drug or genetic material carriers. The lipids composition and the physicochemical properties of the lamella would play an important role in this fusogenic process. Some of the properties that influence this process are the lipid packing, the curve grade, the defect on the external layer and changes in the fluidity of the membrane. In this context the present work intends to study the fusion phenomena in vesicle-vesicle models, trying to relate if the presence of microdomains or defects, mediated by minute changes of the composition affects the fusion process.

In order to determining the efficiency of the fusion in models systems, in which their physicochemical properties have already been described (data not shown), the diminution of the relation excimer/monomer of probes derivate from pyrene was measured. In the carrier vesicle the pyrene shows a major excimer-monomer ratio and by fusing and diluting this ratio decreases. This diminution is proportional to the efficiency of the fusion.

A lipids ternary mixture system, DPPC:DOPC:CHO, was used to determine the fusogenic efficiency. Our data shows that even in absence of fusogenic agents there is a vesicle fusion with efficiency of approximately 50%. Growing concentration of cholesterol affects such efficiency, showing a non-monotonic behaviour. It can be noted that the concentration of cholesterol in which super lattice theory predicts a major proportion of ordered domains and by which a higher rise defects, its presents the higher fusion efficiency of the studied model. These results could indicate that the presence of defects in the lateral order of lipids plays an important role in the fusion process.

This work was support by FONDECYT N° 11090443 (Proyecto Iniciación F.Cuevas)

P30

ELECTRON TRANFER FROM EDTA TO TRIPLET STATES OF PTERINS

María L. Dántola[1], Mariana Vignoni[1], Constanza González[1], Carolina Lorente[1] and Andrés H. Thomas[1]

[1]Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Dep. Química, Facultad de Cs. Exactas, UNLP, CCT La Plata-CONICET. CC 16, Sucursal 4, (1900) La Plata, Argentina. athomas@inifta.unlp.edu.ar

Keywords: pterins, photoinduced electron transfer, superoxide radical

Pterins, a family of heterocyclic compounds, are present in biological systems in multiple forms and play different roles ranging from pigments to enzymatic cofactors for numerous redox and one-carbon transfer reactions.[i] Upon excitation with UV-A radiation, pterins are able to photoinduce DNA damage. The mechanism involved in this process was proposed to be an electron transfer with the subsequent formation of the biomolecule radical cation and a pterin radical anion. In this mechanism the photosensitizer is not consumed. In contrast, it has been suggested that some pterins in the presence of electron donors undergo photoreduction, yielding the corresponding dihydropterin derivative, which in turn is reduced to a tetrahydropterin.[ii]

The present work is aimed to get a better understanding of photoinduced electron transfer mechanisms wherein 6-methylpterin (Mep) act as photosensitizers and ethylenediaminetetraacetate (EDTA) act as electron donor (D). The experiments were performed in slightly acidic aqueous solution under UV-A radiation. We investigated the production of H_2O_2, the effect of dissolved O_2 in the efficiencies of the processes and the experimental conditions needed to achieve photoreduction of Mep.

Under anaerobic conditions, Mep in the presence of EDTA undergoes photoreduction, yielding 6-methyl-7,8-dihydropterin (H_2Mep). However, in air-saturated solutions this reduction does not take place; instead of that, the Mep radical anion reduces O_2 into superoxide radical ($O_2^{\bullet -}$), which eventually dismutates into H_2O_2. Experiments in the presence of selective quenchers suggested the participation of Mep triplet state as electron acceptor. The specific mechanism proposed for these photosensitized reaction is summarized in Equations 1-7.

$$\mathrm{Mep} \xrightarrow{h\nu} {}^1\mathrm{Mep}^* \tag{1}$$

$$ {}^1\mathrm{Mep}^* \longrightarrow {}^3\mathrm{Mep}^* \tag{2}$$

$$ {}^3\mathrm{Mep}^* + O_2 \longrightarrow \mathrm{Mep} + {}^1O_2 \tag{3}$$

$$ {}^3\mathrm{Mep}^* + \mathrm{D} \longrightarrow \mathrm{Mep}^{\bullet -} + \mathrm{D}^{\bullet +} \tag{4}$$

$$ \mathrm{Mep}^{\bullet -} + \mathrm{D}^{\bullet +} \longrightarrow H_2\mathrm{Mep} + \mathrm{D(-2H)} \tag{5}$$

$$ [\mathrm{Mep}^{\bullet -} + \mathrm{D}^{\bullet +}] \longrightarrow [\mathrm{HMep}^{\bullet} + \mathrm{D(-H)}^{\bullet}] \tag{5a}$$

$$ [\mathrm{HMep}^{\bullet} + \mathrm{D(-H)}^{\bullet}] \longrightarrow H_2\mathrm{Mep} + \mathrm{D(-2H)} \tag{5b}$$

$$ \mathrm{Mep}^{\bullet -} + O_2 \longrightarrow \mathrm{Mep} + O_2^{\bullet -} \tag{6}$$

$$ 2\,H^+ + 2\,O_2^{\bullet -} \longrightarrow H_2O_2 + O_2 \tag{7}$$

---

[i] Kappock T. J. and Caradonna J. P. *Chemical Reviews,* 1996, **96**, 2659.

[ii] Kritsky, M. S.; Lyudnikova, T. A.; Mironov, E. A.; Moskaleva, I. V. *J. Photochem. Photobiol. B* **1997**, *39*, 43.

P31

Folic acid oxidation photoinduced by aromatic pterins

M. Laura Dántola, Beatriz Zurbano, Carlos Sebastián Gimenez, Carolina Lorente and Andrés H. Thomas

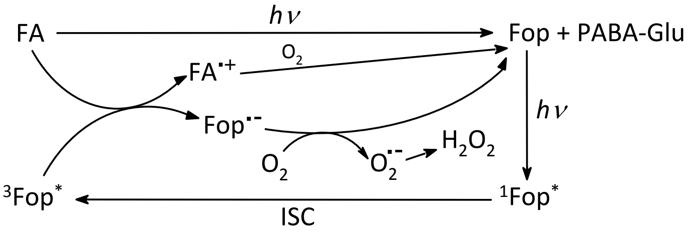
INIFTA, Dep. de Química, Fac. de Ciencias Exactas, Universidad Nacional de La Plata, CCT La Plata-CONICET. C.C. 16, Suc. 4, (1900) La Plata, Argentina. E-mail: athomas@inifta.unlp.edu.aril

Palabras clave: Folic acid, photosensitization, electron transfer

Folic acid (FA) is a vitamin that participates in several metabolic pathways. Its chemical structure consists of a pterin ring system, a *p*-aminobenzoic acid portion, and the amino acid glutamic acid. Interest in the photochemistry of FA has increased since it was demonstrated that, in human beings, UV-A exposure causes its degradation.[1] Moreover, it has been proposed that human skin pigmentation is a mechanism of defense that prevents photolysis of folic acid.[2] Upon UV-A irradiation in the presence of O_2, FA is broken and oxidized yielding 6-formylpterin (Fop) and *p*-aminobenzoyl-glutamic acid (PABA-Glu) as products. It has been observed that when an air-equilibrated aqueous solution of FA is irradiated, the rate of reactant oxidation increases as a function of irradiation time.[3,4] In spite of the importance of the photochemical reaction, the mechanism of this accelerated process remains unknown.

In this contribution we present a study of the photooxidation of FA in the presence of aromatic pterins. The experiments were performed under steady UV-A irradiation in air-equilibrated aqueous solutions at pH in the range 5-6. The irradiated solutions were analyzed by spectrophotometry, HPLC and determination of H_2O_2. Additional experiments were carried out in the presence of triplet state quenchers and superoxide dismutase.

Evidence obtained indicates that aromatic pterins photoinduce the oxidation of FA. Results suggest that electron transfer from FA to the photosensitizer takes place. The FA radical cation yields oxidized products, whereas photosensitizer radical anion reduces dissolved O_2 to form $O_2^{\bullet-}$, which finally generates H_2O_2. In the light of the overall data obtained, the mechanism shown in the scheme is proposed to explain the autoacceleration of the FA photolysis.



References

1 R. F. Branda, J. W. Eaton, *Science* **201**, 625 (1978).
2 N. G. Jablonski, G. Chaplin, *J. Human Evolution* **39**, 57 (2000).
3 A. H. Thomas *et al*, *J. Photochem. Photobiol. A* **135**, 147 (2000).
4 M. K. Off *et al*, *J. Photochem. Photobiol. B* **80**, 47 (2005).

P32

GENERATION OF REACTIVE OXYGEN SPECIES BY X-RAY IRRADIATED SILICON NANOPARTICLES AND ITS RELEVANCE IN TUMOR CELL SURVIVAL.

P. M. David Gara[1,2], N. I. Garabano[1,3], M.J. Llansola Portolés[2], A. Rubert[2], D. O. Mártire[2], O. R. Casas[1], V.N. Sanchez[4], M.C. Gonzalez[2] y M. L. Kotler[1,3].

[1] CITOMA-CIO La Plata, Av. 60 N° 480 (1900) La Plata, Argentina. dgara@inifta.unlp.edu.ar
[2] INIFTA, FCE, UNLP, CC16 Suc 4 (1900) La Plata, Argentina. gonzalez@ inifta.unlp.edu.ar
[3] Dpto. Qca. Biol., FCEN, UBA, 4 Piso, Pab. II (1428) Capital, Argentina, kotler@qb.fcen.uba.ar
[4] Inst. de Biol. Cel.y Neurocs, FMed., UBA, Paraguay 2155 (1121) Capital, Argentina

Keywords: reactive oxygen species, silicon nanoparticles, X-ray irradiation.

Silicon nanoparticles (Si-NP) of 1-10 nm size show strong photoluminescence due to quantum confinement, being wavelength emission dependent on size and surface coating. Their strong luminescence and photostability make them excellent candidates as specific markers in biological environments for "in vitro" and "in vivo" applications. In the present work we study the incorporation of Si-NP to tumor cells, its cytotoxicity and the effect of ionizing radiation on the Si-NP properties and reactive oxygen species (ROS) generation.

Aqueous suspensions of derivatized and naked Si-NP were irradiated with X-rays (electron linear accelerator Varian Clinac, 4 MeV). The absorbed doses were similar to those used in patients with a standard fractionation scheme. Irradiation increased oxidation and decreased the size of Si-NP.

The ability of NP-Si to generate reactive ROS and its steady-state concentration were determined following the consumption of specific probes by HPLC. It was observed that ROS generation was of a higher magnitude order in the presence than in the absence of NP-Si.

The incorporation of naked and derivatized NP-Si to rat glioma C6 cells was demonstrated by microscopy and spectrofluorometry at different incubations times. Subcellular localization of Si-NP was determined by using fluorescent dyes that specifically stain mitochondria (Mitotracker Red CMXRos) and lysosomes (LYSO Tracker Red DND99). Both types of NP-Si were early localized in lysosomas.

Si-NP cytotoxicity was determined both in the presence and absence of ionizing radiation by morphological analysis and cell viability measurement (Neutral Red, Crystal Violet and LDH). The morphological evaluation showed signs of cellular stress with necrotic characteristics at 50µg/ml, in agreement with viability tests. When cells with Si-NP were irradiated with 1Gy, the decrease in cell viability was approximately 40% (20% higher than the corresponding to 2Gy).

The ability of Si-NP incorporated into C6 cells to generate ROS by irradiation was studied employing the DCFH-DA probe. It was observed that ROS generation is a function of both, Si-NP concentration and irradiation doses.

P33

OXIDATION OF 2'-DEOXYADENOSINE 5'-MONOPHOSPHATE PHOTOINDUCED BY LUMAZINE.

M. Paula Denofrio, Andrés H. Thomas and Carolina Lorente

INIFTA, Departamento de Química, Facultad de Ciencias Exactas, Universidad
Nacional de La Plata, CONICET. Casilla de Correo 16, Sucursal 4, 1900- La Plata,
Argentina.E-mail: clorente@inifta.unlp.edu.ar

Keywords. Photosensitization; lumazine; electron transfer

UV radiation induces damages to the DNA molecule and its components through photosensitized reactions. Among these processes, photosensitized oxidations may occur through electron transfer or hydrogen abstraction (type I mechanism) and/or the production of singlet molecular oxygen ($^1O_2$) (type II mechanism). Lumazines are an important family of heterocyclic compounds present in biological systems as biosynthetic precursors and/or products of metabolic degradation.

To evaluate the capability of lumazines to act as photosensitizers through type I mechanism, we have investigated the oxidation of 2'-deoxyadenosine 5'-monophosphate (dAMP) photosensitized by lumazine (pteridine-2,4(1,3*H*)-dione; Lum) in aqueous solutions under UV irradiation. The photochemical reactions were followed by UV/VIS spectrophotometry, HPLC, electrochemical measurement of dissolved O_2 and an enzymatic method for H_2O_2 determination.

Mechanistic analysis indicates that the acid form of Lum (pH=5.5) photoinduces the degradation of dAMP by an electron transfer process. In this mechanism, the excitation of Lum is followed by an electron transfer from dAMP molecule to the Lum triplet excited state, leading to the formation of the corresponding ion radicals ($\text{Lum}^{\bullet-}$ and $\text{dAMP}^{\bullet+}$). In the following step, the electron transfer from $\text{Lum}^{\bullet-}$ to O_2 regenerates Lum and forms the superoxide anion. The latter may disproportionate with its conjugated acid ($HO_2^{\bullet}$) to form H_2O_2 or react with $\text{dAMP}^{\bullet+}$ to regenerate dAMP.

In contrast, no evidence of a photochemical reaction induced by the basic form of Lum (pH 10.5) was observed.

References.

Foote, C. S. *Photochem. Photobiol.* **1991**, *54*, 659

Denofrio, M. P.; Thomas, A. H.; Braun, A. M.; Oliveros, E.; Lorente, C. *J. Photochem. Photobiol. A: Chem.* **2008**, *200*, 282

P34

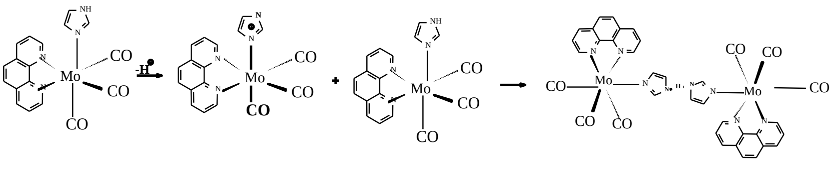
PROPRIEDADES TÉRMICAS E FOTOQUÍMICAS DO COMPLEXO *FAC*-MO(CO)$_3$(PHEN)(IMIDAZOL): ESPECTROSCOPIA UV-VIS, IV, RMN ^{1}H E CALCULOS COMPUTACIONAIS DE DFT

Yuri Dezotti*, Inara de Aguiar*, Guilherme Luiz Chinini*, Rose Maria Carlos*

* Departamento de Química, Universidade Federal de São Carlos, São Carlos, Brasil,
rosem@ufscar.br

Palavras Chaves: Complexos de Mo(0), fotoquímica, DFT.

Diante da busca por novas fontes renováveis de energia, a energia solar se mostra uma forte alternativa e a tecnologia de pigmentos fotossensíveis, um desafio. Assim, os complexos de manganês (I) têm sido alvo de muitas pesquisas, devido à variação de seus estados redox, a reatividade química e suas propriedades fotoquímicas e fotofísicas. Na pesquisa por novos centros metálicos iniciamos estudos com complexos de molibidênio (0). Neste trabalho, é descrito a síntese, caracterização, propriedades espectroscópicas e fotoquímicas do complexo *fac*-Mo(CO)$_3$(phen)(imidazol), 1,10-fenantrolina (phen). Calculos teóricos a nivel de DFT também foram realizados para validar os resultados experimentais. O complexo *fac*-Mo(CO)$_3$(phen)(imidazol), foi obtido a partir do complexo precursor Mo(CO)$_6$. A coordenação com a phen foi confirmada por espectroscopia de IV em CH$_3$CN, onde as bandas referentes às carbonilas são alteradas devido ao abaixamento de simetria de O_h no complexo hexacarbonil (2004, 1973 e 1952 cm^{-1}) para c_s no complexo facial tricarbonil (1892 e 1779 cm^{-1}). O espectro de absorção em CH$_3$CN do complexo tricarbonil apresenta uma banda em 504 nm. O complexo formado apresentou reação térmica pronunciada, com alteração de coloração de roxo intenso para amarelo quando mantido no escuro em solventes coordenantes e na ausência total de luz e atmosfera de N$_2$, caracterizada espectroscopicamente. O estudo cinético avaliado tanto por UV-vis quanto IV mostrou o desaparecimento da banda em 504 nm; 1892, 1779 cm^{-1}, para 460 nm; 2010, 1898, 1877 e 1829 cm^{-1}. Sugerindo a formação de uma nova espécies. O espectro de RMN em CD$_3$CN apresentou os sinais referentes aos prótons do imidazol em 6.27, 6.66 e 7.13 ppm além dos prótons da espécie gerada térmica e fotoquimicamente em 7.02 e 7.57 ppm, indicando a formação de uma nova espécie contendo o íon imidazolato. Os estudos fotoquímicos realizados com irradiação em 420 nm levaram a formação dos mesmos produtos obtidos termicamente, mas com tempo de reação inferior (60% em 2 horas e 71% em 10 minutos de irradiação). As geometrias das espécies formadas durante os processos, térmico e fotoquímico, foram otimizadas usando cálculos computacionais de DFT e confirmaram o mecanismo para a reação térmica e fotoquímica descrito abaixo. Os dados são relevantes para possível aplicação deste complexo em reações de transferência de elétrons.



P35

VISIBLE LIGHT SUPEROXIDE RADICAL ANION GENERATION BY TETRA(4-CARBOXYPHENYL)PORPHYRIN/TIO_2: EPR CHARACTERIZATION

Carlos E. Diaz-Uribe[1,2], Martha C. Daza[1], Fernando Martínez O.[2], Edgar A. Páez-Mozo[2], Carmen L. B. Guedes[3] and Eduardo Di Mauro[3]

[1] Grupo de Bioquímica Teórica, Universidad Industrial de Santander, Bucaramanga, Colombia.
[2] Centro de Investigaciones en Catálisis, Universidad Industrial de Santander, Bucaramanga, Colombia.
[3] Laboratório de Fluorescência e Ressonância Paramagnética Eletrônica, LAFLURPE, Universidade Estadual de Londrina, Londrina, PR, Brazil, email: dimauro@uel.br.

Keywords: DMPO; Superoxide anion; Porphyrin; Dye-sensitized TiO_2; Spin trapping.

The generation of superoxide radical anion $O_2^{\bullet-}$ from tetra(4-carboxyphenyl)porphyrin (TCPP) adsorbed on TiO_2 in DMSO and irradiated by visible light was studied using EPR spectroscopy and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as spin trap. A chemical filter was used to remove light with wave lengths >500 nm. A multiline EPR spectrum was observed, characteristic of a mixture of two adducts, the first corresponding to DMPO-$O_2^{\bullet-}$ and the second to the so-called nitroxide-like radical. Hyperfine coupling constants determined for the DMPO-$O_2^{\bullet-}$ adduct are: a_N=14.1 G, a_H^β=10.8 G and a_H^γ=1.4 G, and for the nitroxide-like radical adduct a_N=14 G. An increased intensity of the EPR lines corresponding to the nitroxide-like radical adduct was observed under irradiation without chemical filter, which suggests a possible DMPO-$O_2^{\bullet-}$ decomposition. No singlet oxygen could be detected by EPR spectroscopy using 2,2,6,6-tetramethyl-4-piperidone (TEMP) as spin trap and by chemical trapping using anthracene as the trap.

P36

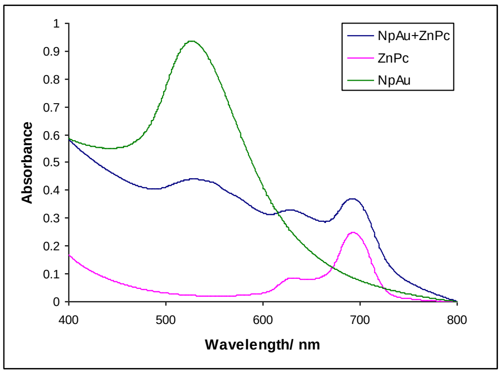
PHTHALOCYANINE-STABILIZED GOLD NANOPARTICLE: A POTENTIAL DELIVERY VEHICLE FOR PHOTODYNAMIC THERAPY

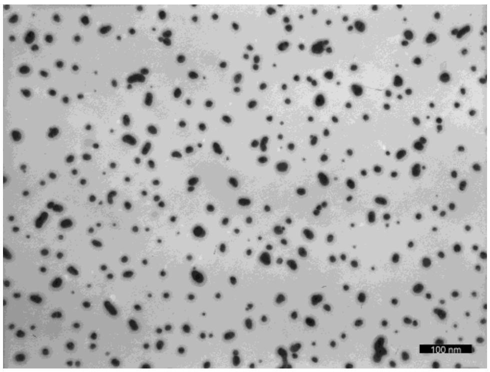
Virginia E. Diz*, María C. García Vior#, Josefina Awruch#, Lelia E. Dicelio*

* INQUIMAE/ Departamento de Química Inorgánica, Analítica y Química Física. Facultad de
Ciencias Exactas y Naturales. Universidad de Buenos Aires, Pabellón II,
C1428EHA, Buenos Aires. Argentina
Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de
Buenos Aires, Junín 956, 1113 Buenos Aires. Argentina
e-mail: led@qi.fcen.uba.ar

Keywords: Gold nanoparticles, thiol-phthalocyanine, synthesis.

In the fast-developing field of nanotechnology, Au nanoparticles have served as a versatile platform for exploring many aspects of basic science. Metalic nanoparticles have been modified by a great deal of organic functional groups to stabilize them[1].The great interest in the development of those systems led us to synthesize macrocyclic phthalocyanine ligands protect Au nanoparticles. To obtain stable SPc-protecting Au nanoparticles we focussed on gold nanoparticles formed through multidentate ligation using the macrocyclic phthalocyanine thioester derivative *tetrakis*[(3-acetylsulfanyl)-propoxy]phthalocyaninatozinc(II) (SPc)[2] from by ligand-exchange reactions from citrate-protected Au nanoparticles according to the Slot[3] method. After ligand exchange, the nanoparticles became insoluble in water though soluble in N,N-dimethylacetamide thus indicating that ligand exchange was accomplished. The functionalized Au nanoparticle have suitable properties for singlet oxygen photoproduction as second generation photosensitizer for photodynamic therapy (PDT). The visible absorption spectrum of the Pc-coated gold nanoparticle shows a typical Au plasmon bandwith at 525 nm and a Q-band at 693 nm corresponding to phthalocyanine-coordinated Au nanoparticle. Transmission electron micrographs of the Citrate-capped Au nanoparticles ranging between 7 and 26 nm are consistent with those previously reported by several groups.





TEM images of Citrate-capped Au nanoparticles (scale:100nm)

:s, L.D. *Rep. Prog. Phys.*, **1994**, 57, 603,.2. García Vior, M.C. *Tetrahedron Lett.*, **2009**, 50, 2467,.3. Slot, J.W. *Eur.J.Cell.Biol..*, **1985**, 38, 87.

P37

CONFOCAL MICROSCOPY FOR INVESTIGATION OF POLYFLUORENE DERIVATIVES SORPTION ONTO REGENERATED CELLULOSE FIBERS

Raquel A. Domingues[*], **Teresa D. Z. Atvars**[*]

Departmento de Físico-Química, Instituto de Química, Universidade Estadual de Campinas, Campinas, Brazil, P.O. Box 6154, 13084-971, SP, Brazil, e-mail: rdomingues@iqm.unicamp.br

Keywords: cellulose, polyfluorene, confocal microscopy

Confocal microscopy is an optical imaging technique used to increase optical resolution and contrast of a micrograph by using point illumination and a spatial pinhole to eliminate out-of-focus light in specimens that are thicker than the focal plane.[1]

The method of image formation in a confocal microscope is fundamentally different from that in a conventional wide-field microscope in which the entire specimen is bathed in light from a mercury or xenon source, and the image can be viewed directly by eye. In contrast, the illumination in a confocal microscope is achieved by scanning one or more focused beams of light, usually from a laser, across the specimen. The images produced by scanning the specimen in this way are called optical sections. This refers to the noninvasive method of image collection by the instrument, which uses light rather than physical means to section the specimen.[2]

Using this described technique, in the present work was studied poly(fluorene) derivatives, poly[9,9-dioctylfluorenyl-2,7-diyl)-co-1,4-benzo-{2,1’-3}-thiadiazole)] and Poly[9,9-di-(2-etillhexil)-fluorenil-2,7-diil] end capped with 2,5-difenil-1,2,4-oxadiazol sorbed onto two different cellulose fibers: one without previous treatment and other treated with a silane surface modifier. It was possible to verify point-to-point how the probe was distributed and quantify detailed the emission intensity. Since the confocal microscopy is enabled to automate the collection of threedimensional (3D) data in the form of Z-series, it was also studied the polyfluorenes distribution in Z-axes of fiber.

The optimization of time sorption was obtained measuring the fluorescence intensity of emitting polymer solution during the sorption, since a decrease in solution concentration indicates an increase of polymer sorption. The sorbed material was also characterized by epifluorescence and scanning electronic microscopy. Using epifluorescence microscopy a uniform emission was observed for both samples and no significant difference in emission occurred.

Work supported by FAPESP, INEO.

[1] E. Lang, J. Baier e J. Köhler, J. Microsc., 222, 118 (2006)

[2] Methods in Molecular Biology, vol. 122: Confocal Microscopy Methods and Protocols Edited by: S. Paddock Humana Press Inc., Totowa, NJ.

P38

PHOTODEGRADATION OF INDOL COMPOUNDS SENSITIZED BY FLAVINS IN UNILAMINAR VESICLES

A. M. Edwards, C. Bueno, E. Alarcón

Departamento de Química Física, Pontificia Universidad Católica de Chile
aedwards@puc.cl

Key Words: flavins, indole derivatives, unilaminar vesicles

Riboflavin (RF), commonly called Vitamin B_2, can act as a photochemical sensitizer, provoking the photodegradation of molecules that do not absorb visible light. In aqueous solutions and in the presence of oxygen, RF leads to substrate oxidation through generation of singlet oxygen (type II mechanism) and via radical species (type I mechanism). RF-Trp photoproducts are toxic to human and mouse tumour cells. In a previous work performed by our group, we studied the photochemical and pharmacokinetic properties of flavins esters (FE). The results showed that flavin esters are more stable to visible light irradiation than RF. The different flavins derivatives showed important differences in their photochemical and pharmacokinetic properties. RF, LF and the shorter-chain RF esters were rapidly cleared from the serum, however, the longer-chain esters exhibited a prolonged retention. Hence, it is important to study the photochemical behaviour of RF and FE in systems that mimic membrane models, because it is known that photophysical and photochemical processes in compartmentalized systems could differ from those in homogeneous medium.

In this work, we study the incorporation of flavinic and indolic derivatives in small unilaminar vesicles (SUV) of DPPC, and the effect of their incorporation in the photodegradation rate of indolic derivatives sensitized by flavins.

The incorporation of indolic and flavinic compounds were determinated by different methods. On the basis of the shift to shorter wavelength of the absorption and fluorescence bands of indole derivates we can infer that Trp was localized into the intravesical aqueous phase, while the most hydrophobic indolic compounds (NATE; NATA; indol-3-acetamide) were localized in the lipid-aqueous interphase. According to the position of the emission band, RF and LF are localized in the aqueous compartment of the vesicles. Otherwise, a 20 nm blue shift in the absorption and 2 nm in the fluorescence spectra, respectively, was observed for TPRF, indicating that it is localized in the lipid interphase.

The pseudo first order rate constants values for the indole derivatives photodegradation sensitized by flavins show that when TPRF was used as photosensitizer, the photodegradation in SUV was greater than in homogeneous medium for all the indole derivatives.

P39

DEGRADACIÓN DE LOS PESTICIDAS FENÓLICOS DICLOROFEN Y BROMOXINIL, MEDIADA POR LUZ ULTRAVIOLETA Y VISIBLE

Juan Pablo Escalada[1], Adriana Pajares[1], José Gianotti[1], Alicia Biasutti[2], Patricia Molina[2], Walter Massad[2], Francisco Amat-Guerri[3] y Norman A. García[2].

[1]Unidad Académica Río Gallegos, Univ. Nac. de la Patagonia Austral, 9400 Río Gallegos, Argentina
[2]Departamento de Química, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina. ngarcia@exa.unrc.edu.ar
[3]Instituto de Química Orgánica General. CSIC. 28006 Madrid. España

Palabras Clave: Bromoxinil, Diclorofen, Fotodegradación.

La fotoirradiación sensibilizada de los pesticidas fenólicos Bromoxinil (BXN) y Diclorofen (DCP), bajo condiciones aeróbicas, produce una oxidación relativamente eficiente de los mismos en un proceso que incluye también la degradación del fotosensibilizador, riboflavina. Los pesticidas elegidos, que solamente absorben luz ultravioleta, exhiben algunas propiedades químicas que los diferencian de los fenoles comunes: BXN posee un valor de pK_a extremadamente bajo para la ionización del OH fenólico, mientras que DCP es un compuesto bifenólico, con uno de sus pK_a relativamente bajo también. Un estudio detallado de la cinética y mecanismos, empleando fotólisis continua de luz visible, detección polarográfica de consumo de oxígeno, espectroscopía fluorescente estacionaria y resuelta en el tiempo, detección de fosforescencia resuelta en el tiempo y técnicas de láser flah fotólisis, indica que las especies H_2O_2 y oxígeno singlete molecular ($O_2(^1\Delta_g)$) son responsables del procesos oxidativos en ambos pesticidas. Se observó una alta eficiencia y un moderado efecto micelar sobre la reacción mediada por $O_2(^1\Delta_g)$. La fotoirradiación ultravioleta a 254 nm degrada el BXN y el DCP con rendimientos cuánticos de 0.18 and 0.05 respectivamente.

Las estructuras químicas de DCP y muy especialmente BXN resultan de gran interés a la hora del diseño de pesticidas fotodegradables en condiciones típicas medioambientales, es decir en un medio aeróbico acuoso ligeramente ácido, bajo fotoirradiación con luz visible y en presencia de sensibilizadores presentes en cursos de agua naturales.

P40

A FLASH PHOTOLYSIS STUDY OF THE TRIPLET STATE QUENCHING OF MACROPHOTOINITIATORS BASED ON THIOXANTHONE BY AMINES

Ricardo Augusto Escriptório,[1] **Beatriz Eleutério Goi,**[2] **Carla Cristina Schmitt Cavalheiro**[1]**, Miguel Guillermo Neumann**[1]

1 Instituto de Química de São Carlos/USP, São Carlos, Brazil, Av. Trabalhador são carlense, ricardoffice@yahoo.com.br
2 Departamento de Física, Química e Biologia, Unesp, Presidente Prudente, Brazil, Rua Roberto Simonsen, goibeatriz@gmail.com

Key Words: Macrophotoinitiators; Polimerization

The present work is devoted to the investigation of excited state processes of macrophotoinitiators of polymerization. As macroprohoinitiator were used BMA-co-TXa and HMa-co-TXa. Also measurements of low molecular weight analogues were carried out in order to compare. The concentration of photoinitiators is 2.3.10^{-4} *M* with reference to thioxanthone moieties. The amines are: Ethyl 4-dimethylaminobenzoate (EDB), tryethylamine (TEA), 2-(Dimethylamino) ethyl methacrylate (DMAEMA) and 2-(Diethylamino) ethyl methacrylate (DEAEMA). Table 1 summarizes the data obtained from laser spectroscopy measurements with third harmonic (355nm).

Table 1: Values of triplet lifetime ($^3\tau_0$) and bimolecular rate constant (^3k_q).

Compounds/amines	**EDB**	**TEA**	**DMAEMA**	**DEAEMA**
	k_q (M^{-1}.s^{-1})	k_q (M^{-1}.s^{-1})	k_q (M^{-1}.s^{-1})	k_q (M^{-1}.s^{-1})
Thioxanthone (τ_0=2.5μs)	6.5×10^9	3.0×10^9	1.0×10^9	1.0×10^9
BMa-co-TXa (τ_0=2.6μs)	3.5×10^9	1.5×10^9	8.5×10^8	6.5×10^8
HMa-co-TXa (τ_0=2.1μs)	4.0×10^9	2.0×10^9	8.5×10^8	7.0×10^8

As can be seen in Table 1, ^3k_q of EDB for thioxantone is higher than that of macrophotoinitiators. Besides that, in all amines used thioxanthone is highest than that macrophotoinitiators. The values of ^3k_q followed the order: EDB > TEA > DMAEMA > DEAEMA.
The values of ^3k_q for macrophotoinitiators are practically the same when compared with same amine. These results can be used as base in study of photopolymerisation.

(CNPq, FAPESP)

P41

ESTUDIOS FOTOQUÍMICOS DE LA UNIÓN DE DERIVADOS DE 1,4-DIHIDROPIRIDINAS A LA ALBÚMINA DEL SUERO HUMANO

Pamela Espinoza, María Victoria Encinas, Emilio Cardemil,

Departamento Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago, Santiago, Chile. E-mail: pamelaespinozasommer@gmail.com

Palabras clave: HSA, 1,4-dihidropiridinas, apagamiento de fluorescencia.

La albúmina del suero humano (HSA) está involucrada en el transporte de ligandos en la circulación sanguínea. Esta proteína une una amplia variedad de drogas, principalmente en sus dominios II y III, haciendo que esté implicada en la distribución y efectividad terapéutica (1). En este trabajo estudiamos la unión de derivados de 1,4-dihidropiridinas (DPH) con diferentes sustituyentes en la posición 4 a la HSA, usando técnicas espectroscópicas de fluorescencia. Estas drogas son bloqueadoras de los canales de calcio, por lo cual son ampliamente usadas en el tratamiento de la hipertensión (2). Los estudios de unión de las drogas a la proteína HSA se realizaron usando como prueba fluorescentes el único triptófano de la HSA (Trp-214), ubicado en el subdominio IIA (3). Los estudios del efecto del agregado de las drogas tanto en la intensidad de fluorescencia como en el tiempo de decaimiento mostraron que la desactivación de la fluorescencia de la proteína por las diferentes drogas es un proceso estático. Las constantes de asociación son del orden de 10^4 M^{-1}, variando con la estructura del sustituyente en la posición 4. La mayor afinidad se encontró para la DHP sustituida con el sustituyente 2,3-diclorofenilo, sugiriendo la importancia de factores estructurales, en particular interacciones hidrofóbicas. Para sustituyentes iónicos la unión no es afectada por la fuerza iónica, indicando la ausencia de interacciones electrostáticas. Para todas las drogas estudiadas, la estequiometría de unión fue de 1:1.

Experimentos de desplazamiento usando warfarina, la cual se une al subdominio IIA (4), mostraron que las DHP se unen en este sitio. Las constantes de asociación determinadas a pH 4 también sugieren que las drogas se unen en el subdominio IIA. Los cálculos utilizando transferencia de energía de fluorescencia (FRET) dieron una distancia Trp-droga de 20Å, lo que concuerda con la unión de las drogas al subdominio IIA de la HSA.

(1) Kragh-Hansen U.; Tuan Gian V.; Otagiri M. (2002) *Biol. Pham. Bull. 25, 695-704*

(2) Pontremoli R.; Leoncini G.; Parodi A. (2005) *Expert Rev. Cardiovasc. Theor.* 3, 43-50.

(3) Min He X.; Carter D. (1992). *Nat.* 358, 209-215.

(4) Petitpas I.; Bhattacharya A.; Twine S.; East M.; Curry S. (2001) *J. Biol. Chem.* 276, 22804-22809.

Financiado por: FONDECYT 1070123, beca doctorado CONICYT, proyecto doctorado CONICYT AT-24090003.

P42

EFECTO DE LA PROTONACIÓN Y/Ó COORDINACION DE CU(II) SOBRE LA LUMINISCENCIA DE UN COMPLEJO DE RENIO(I)

Ulises N. Fagioli, Gustavo T. Ruiz, Mario R. Féliz y 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

Palabras clave: luminiscencia, protonación, piracina

Los complejos de metales del grupo del platino, particularmente Ru(II), Os(II), y Re(I) han despertado un gran interés debido a sus fuertes absorciones en la región visible del espectro, a su buena estabilidad fotoquímica, eficiente luminiscencia y a sus estados excitados (generalmente causantes de la luminiscencia) de transferencia carga desde el metal y hacia el ligando (MLCT), de vida relativamente larga. Este interés está basado, en parte, en los esfuerzos dirigidos a diseñar y construir sistemas multicomponentes capaces de llevar a cabo funciones inducidas por la luz y/ó especies redox que sean de utilidad práctica, como por ejemplo en el diseño y el uso de materiales luminiscentes como sondas y sensores.[1] Algunos ejemplos incluyen fibras ópticas basadas en sensores luminiscentes aptos para la detección ó medición de O_2, pH, CO_2, temperatura o aplicados en el área de los inmuno-ensayos. Típicamente la información deseada se puede obtener a partir de cambios en la intensidad, en el tiempo de vida o en la distribución espectral de la luminiscencia.

En el presente trabajo se estudia el efecto que tiene la protonación de la piracina y/ó la coordinación de CuX_2 (X= Cl^-, $CF_3SO_3^-$) a la misma sobre la luminiscencia estacionaria y resuelta en el tiempo del complejo (2-piracina)-CO_2-$Re(CO)_3$(2,2´bipiridina) con el objetivo de evaluar su posible aplicación en la fabricación de un sensor capaz de detectar trazas de este metal de transición y/ó medir el pH de una solución. Los efectos que tiene la protonación y/ó la coordinación de $Cu(CF_3SO_3)_2$ sobre la luminiscencia del complejo $pzCO_2Re(CO)_3(bpy)$ son muy marcados: se observa un aumento de la intensidad de emisión (unas 20 veces) y un corrimiento del máximo de emisión a longitudes de onda menores. En experimentos de flash fotólisis con λ_{ex} = 351nm, cuando se excita opticamente al complejo Pyr-CO_2-$Re(CO)_3$(bpy) se observa, a tiempos cortos (35 ns después del pulso del laser) el espectro del estado excitado de transferencia de carga del metal al ligando MLCT(Re→bpy). El decaimiento de este transiente es biexponencial, siendo el proceso correspondiente al tiempo más corto, el de mayor peso en los factores pre-exponenciales. Cuando el mismo experimento se lleva a cabo en presencia de $Cu(CF_3SO_3)_2$ ó H^+, en condicioines de saturación de los grupos acínicos de la piracina, el espectro del transiente observado es similar al que se observa en ausencia de $Cu(CF_3SO_3)_2$ ó H^+, aunque ahora el decaimiento es monoexponencial y ha desaparecido el proceso rápido (correspondiente al estado excitado MLCT(Re→bpy)), quedando solo el transiente de vida más larga. Este transiente puede ser asignado a una transferencia de carga del Re al grupo carboxilato (MLCT(Re→$pzCO_2$)). Estos resultados concuerdan muy bién con los obtenidos de los decaimientos de la emisión resuelta en el tiempo.

P43

PRODUCCIÓN DE ANIÓN SUPERÓXIDO POR UNA ANTRAQUINONA DE ORIGEN NATURAL

Fernández Ivana[1], Comini Laura[2], Farías Adrián[3], Konigheim Brenda[3], Rivarola Viviana[1], Cabrera José[2] y Núñez Montoya Susana[2].

[1] Dpto. Biol. Mol., Fac. Cs. Exs. FQca. y Nat. Univ. Nac. Río Cuarto. Río IV, Arg.
[2] Farmacognosia, Fac. Cs.Qcas., Univ. Nac. Córdoba, IMBIV-CONICET. Cba., Arg.
[3] Instituto Virología, Fac. Cs. Médicas, UNC. Ciudad Universitaria (5016) Córdoba, Argentina.
E-mail: lcomini@fcq.unc.edu.ar

Palabras claves: ω-metil éter de lucidina, *Heterophyllaea pustulata*, Fotosensibilizantes

A partir de las hojas y tallos de *Heterophyllaea pustulata* Hook. f. (Rubiáceas) se han aislado principalmente derivados antraquinónicos[1, 2], cuyas propiedades fotosensibilizantes han sido establecidas por nuestro grupo de trabajo[3, 4]. Asimismo, hemos demostrados que las antraquinonas (AQs) predominantes serían las responsables del efecto fototóxico de este arbusto[5], ya que provoca dermatitis y ceguera en los animales que la ingieren y se exponen a la luz solar; razón por la cual, se la conoce popularmente como “cegadera” en las regiones donde habita. Esto es, en la zona cordillerana del NO argentino (2500 y 3000 m. s. m.)

En esta trabajo informamos la purificación e identificación de una AQ presente solo en las raíces de *H. pustulata*: ω-metil éter de lucidina, y se determinó su capacidad para generar anión superóxido ($O_2^{-\cdot}$) *in vitro* cuando es expuesta a la luz UV (fotosensibilización Tipo I).

Para ello, se utilizó un ensayo fotobiológico indirecto que evalúa la reducción de Nitroblue Tetrazolium (NBT) a azul de formazán, por acción del $O_2^{-\cdot}$ producido por leucocitos humanos (2×10^6 cél/ml) en presencia de un agente oxidante (AQs), bajo condiciones de oscuridad y radiación UV (380-480 nm). Esta AQ se ensayo a dos concentraciones diferentes: 10 y 20 µg/ml por duplicado, disuelta en PBS con DMSO como co-solvente (1%). Se incluyeron controles celulares por duplicado, que junto a las muestras fueron incubados a 37 °C durante 30 min, bajo las dos condiciones experimentales (oscuridad y radiación). Se midió la absorbancia del azul de formazán generado en el interior de los leucocitos por espectrofotometría UV-Visible (λ= 575 nm). El incremento en la producción de $O_2^{-\cdot}$ respecto al basal (control celular, 100 %) se expresó en porcentaje.

Según los resultados obtenidos, ω-metil éter de lucidina estimula levemente el metabolismo oxidativo de leucocitos, ya que en oscuridad se observó un aumento en la generación de O_2^{-} $^{\cdot}$del 24,3 ± 0,2 y 35,7 ± 0,3 %, a 10 y 20 µg/ml respectivamente. Bajo radiación, la producción de este anión sufrió un importante incremento a las dos concentraciones ensayadas: 83,3 ± 0,1 y 88,3 ± 0,2 %, respectivamente; lo que implica una fotoestimulación del metabolismo oxidativo.

En conclusión, se demostró que ω-metil éter de lucidina produce fotosensibilización Tipo I *in vitro*, la cual es directamente dependiente de la concentración utilizada.

Bibliografía:
1. SC Núñez Montoya, AM Agnese, C Pérez, IN Tiraboschi, JL Cabrera. (2003) Phytomedicine 10, 569-574.
2. SC Núñez Montoya, AM Agnese, JL Cabrera. (2006) J. Nat. Prod. 69, 801-803.
3. SC Núñez, LR Comini, M Sarmiento, C Becerra, I Albesa, G Argüello, JL Cabrera. (2005) J. Photochem. Photobiol. B 78, 77-83.
4. LR Comini, SC Núñez Montoya, M Sarmiento, JL Cabrera, Gustavo A Argüello. (2007) J. Photochem. Photobiol. A 188, 185-191.
5. SC Núñez Montoya, LR Comini, B Rumie Vittar, IM Fernández, V Rivarola, JL Cabrera. (2008) Toxicon 51 (8), 1409-1415.

P44

DEGRADATION OF PARACETAMOL BY HETEROGENEOUS PHOTOCATALYSIS

Marcela D. França[1], Antonio E. H. Machado[1,2], Paulo S. Muller Jr[3]
[1]Universidade Federal de Uberlândia, Instituto de Química, Laboratório de Fotoquímica,
P. O. Box 563; 38400-902 Uberlândia, MG, Brazil.
[2]Universidade Federal de Goiás, Campus Avançado de Catalão; Catalão, GO, Brazil.
[3]Nanobrax, Soluções Tecnológicas e Prestação de Serviços Ltda.; Uberlândia, MG, Brazil.
E-mail: marceladfranca@yahoo.com.br

In this communication are presented results of a comparative study involving the photocatalytic degradation of paracetamol (*N*-(4-hydroxyphenyl)-etanamide) - a drug with analgesic properties and high hepatotoxic potential, using the titanium oxide P25 and a composite based in the association between titanium oxide and zinc phthalocyanine (Machado et al., 2008; Machado et al., 2004). In the essays, the effluent to be treated (4 L of an aqueous solution containing 10 ppm of paracetamol) was circulated by an annular borosilicate glass reactor with a flow rate of 1345 $mL \cdot min^{-1}$. A mercury vapor lamp, high pressure, 400 W, was placed inside. The catalysts studied (**(1)** Evonick-Degussa TiO_2 P25, and **(2)** TiO_2/Zinc Phthalocyanine composite at 2.5% (Machado et al., 2008; Machado et al., 2004)) were used at the concentration of 100 $mg \cdot L^{-1}$. The experiments were done by adding different concentrations of H_2O_2 at 30%. In all ensaios, the pH of the reaction medium was adjusted to 3.00, and the reaction time limited to 120 minutes. Aliquots were collected at 20 minutes intervals and analyzed in terms of total organic carbon (TOC) and H_2O_2 consumption. The methodology used to estimate the quantum yield of hydroxyl radical production ($\Phi(HO^{\cdot})$) was described in a previous work (Machado et al., 2008). The TOC reduction during the reaction was of 45% and 40% for a H_2O_2 consumption of 39% and 33%, respectively for **(1)** and **(2)**, for an initial concentration of H_2O_2 equal to 8.82 mM – corresponding to 4.00 mL of H_2O_2 30%. Essays done with **(2)** varying the added volume of H_2O_2 suggest that the addition of 0.10 $mL \cdot L^{-1}$ to the effluent is sufficient to warrant a TOC reduction of 42% and a consumption of H_2O_2 equal to 53%. The results indicate that TiO_2/Zinc Phthalocyanine composite presents a superior photocatalytic activity, since its specific surface area (between 35 and 42 g/m^2) is about 30% lower the value reported for TiO_2 P25. The extremely low $\Phi(HO^{\cdot})$ (1% for the TiO_2/ZnPc composite and 6% for TiO_2 P25) suggest that the reactions that lead to paracetamol oxidation should involve a much more complex set of active species and processes. Thus, $\Phi(HO^{\cdot})$ is not a safe parameter to define the photocatalytic activity of TiO_2 and their associations.

Acknowledgement: FAPEMIG, CNPq e Nanobrax.

Machado, A. E. H., França, Marcela D., Velani, Valdemir, Magnino, Gabriel A.,Velani, Hosana M. M., Freitas, Flávio S., Muller Jr, P. S., Sattler, C., Schmuecker, M., *Int. J. Photoenerg.* (online), 2008 (2008) 482373.

Machado, A. E. H., Miranda, J. A., Sattler, C., Oliveira, L. de, WO2004089525-A2, BR200300920-A, Application no. 04726392.6. See also PI 03009203-3 (RPI no. 1793, INPI, 2005).

P45

FOTORREDUCCIÓN DE 3-METIL-QUINOXALIN-2-ONAS POR N-FENILGLYCINA. EVIDENCIA DE REACCIONES RADICALARIAS EN CADENA.

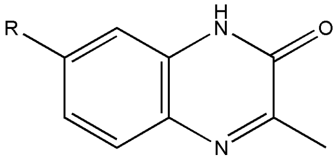
Julio R. De la Fuente[1], Krzysztof Bobrowski[2], Karina Corada[1], Komal Dadlani[1], Alvaro Cañete[3], Christian Aliaga[1].

[1]Fac. Cs. Qcas. Y Farm., Universidad de Chile, email: jrfuente@ciq.uchile.cl
[2]Institute of Nuclear Chemistry and Technology, Warsaw, Poland.
[3]Depto. Qca., Fac. Química, Pontificia Universidad Católica de Chile.

Palabras clave: Quinoxalinonas, aminoacidos, fotorreducción.

En las últimas décadas se han publicado muchos estudios referentes a las propiedades farmacológicas de derivados de quinoxalin-2-onas. En algunos de ellos se localizan las quinoxalin-2-onas en el interior de bolsillos proteicos,[1-3] donde esta podría participar en reacciones de transferencia de electrón con residuos de aminoácidos. Sin embargo, hasta la fecha no hay publicaciones sobre especies transientes generadas por transferencia de electrón fotoinducida desde aminoácidos.

En este trabajo reportamos algunos resultados sobre las fotorreacciones de N-fenilglycina con derivados substituidos en la posición 7- de la 3-metil-quinoxalin-2-ona.



Quinoxalin-2-ones

R = -H; $-OCH_3$; $-CH_3$; $-CF_3$; -CN; -Br; -F

Estos compuestos reaccionan eficientemente con rendimientos cuánticos de fotoconsumo entre 0,1 y 2,5, sugiriendo reacciones radicalarias en cadena después de una primera etapa de transferencia de electrón fotoinducida. Esta primera etapa de la fotorreacción fue confirmada por la identificación del radical anión de las quinoxalin-2-onas en experimentos de láser flash fotólisis en presencia de DABCO y N-fenilglycina y en experimentos de radiólisis de pulso. Los espectros transientes observados son prácticamente idénticos, confirmando la identidad del par ión radical y el radical anión de las quinoxalin-2-onas como la primera especie transiente generada en la fotoreacción.

Agradecimientos: FONDECYT Proyectos N° 1070623, 1100121.

Referencias:

1.Carta, A., et al., M-Rev. in Med. Chem., 2006. 6(11): p. 1179-1200.
3.Ries, U.J., et al., Bio. & Med. Chem. Let. 2003. 13(14): p. 2297-2302.
5.Lawrence, D.S., et al., J. Med. Chem., 2001. 44(4): p. 594-601.

P46

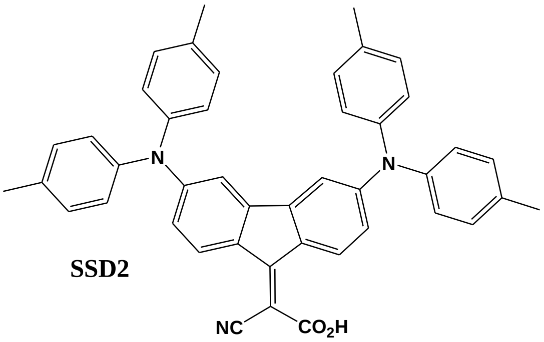
SENSITIZATION OF WIDE BAND GAP OXIDE SEMICONDUCTOR BY FLUORENE BRIDGED DONOR/ACCEPTOR DYE

Miguel Gervaldo,* Lorena Macor,* Daniel Heredia,* Ken-Tsung Wong,[#] Luis Otero* and Fernando Fungo*

\# Department of Chemistry, National Taiwan University, Taipei 106, Taiwan.
* Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal 3 (5800), Río Cuarto, Argentina, e-mail: mgervaldo@exa.unrc.edu.ar

Key Words: Dye, Donor-acceptor, Solar Cells.

The continuous increment of energy demand, and the limited accessibility to traditional sources, drives the development of new materials and devices for solar energy conversion in one of the most important research area. The solar light absorbed by organic dyes can start a process that culminates in the generation of electricity when they form part of a new kind of low-cost solar energy conversion device: dye sensitized solar cells (DSSCs).



SSD2

A promising strategy in the design of highly efficient organic dyes for DSSCs is the linking of organic electron donor/acceptor (DA) systems through conjugated spacers, with the TiO_2 surface anchoring groups (e.g., carboxylate) integrated onto the acceptor moiety. Irradiation of these bipolar molecules generates photoinduced intramolecular charge transfer states, which can inject electrons to the TiO_2 conduction band. The use of long π-conjugated bridges that red-shift the absorption spectrums facilitate the efficient harvesting of solar energy. However, the presence of lengthy rod-like structure can lead to aggregation and, therefore, self-quenching and inefficient electron injection into the TiO_2. These deleterious processes can be avoided, or suppressed, when the dye molecules possess bulky structural features that impede aggregation.

In this study we synthesized and characterized the bipolar dye **SSD2** featuring two diphenylamino (DPA) groups as donors and a 2-cyanoacrylic acid unit as acceptor, with a fluorene bridge ensuring efficient DA interactions. This novel dye possesses several unique features that are potential advantages for application in DSSCs. For example, **SSD2** is composed of two D branches in a molecular structure, which not only increases the light absorption efficiency but also minimizes dye aggregation. The frontier molecular orbitals revealed that the highest occupied molecular orbital (HOMO) of **SSD2** is localized mostly on the diphenylamino groups, whereas the lowest unoccupied molecular orbital (LUMO) is localized on the cyanoacrylic acid units. The energy levels revealing that both, electron injection into TiO_2 from the dye's excited states and dye reduction by the I^-/I_3^- couple are exothermic, making DSSC operation feasible.

P47

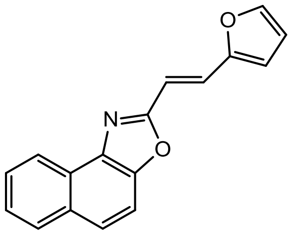
SOLVENT EFFECT ON THE PHOTOPHYSICS OF FURYLNAPHTHOXAZOLE DERIVATIVES

Yasser Gidi, Renzo P. Zanocco, Antonio L. Zanocco

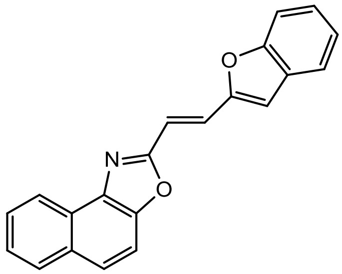
Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Fisicoquímica, Casilla 233, Santiago - 1, Santiago, Chile. e-mail: zanocco@ciq.uchile.cl

Keywords: Fluorescence, Naphthoxazole derivatives, Singlet molecular oxygen

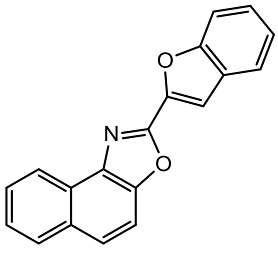
The photophysics of a family benzoxazole and styryl benzoxazoles namely; 2-(4'-R-styryl)benzoxazole, (R = NMe2, 2',4'-OCH3, OCH3, CH3, H, Cl and CN) has been previously investigated in several organic solvents. The absorption and fluorescence characteristics (such as fluorescence maximum, quantum yield and lifetime) are tuned by substitution, solvent and protonation. Depending on the substituent, the benzoxazole ring can be an electron donor (as in the case of R = CN) or an electron acceptor. The protonation constants of the benzoxazole nitrogen atom, in both the ground and excited state, are strongly dependent on substitutent, indicating that the basicity of all derivatives (except for R = CN) increases upon excitation. The trans→cis photoisomerization quantum yields depend on the nature of the substituent and the solvent characteristics like polarity and viscosity. Effects of solvent polarity and viscosity as well as the substituent on both the fluorescence and the isomerization quantum yields, suggested that the two-deactivation pathways are competitive. Building on the fact that the benzoxazole excited states have substantial charge-transfer character, we hypothesized that naphtho- for benzo-ring change could substantially affect the photophysical properties of these compounds. In addition, inclusion of a strongly electron donor substituent could also diminish the fluorescence quantum yield. In this work we report the results of the study of solvent effect on the absorptive and emissive characteristics of compounds in the figure:



(*E*)-2-(2-(furan-2-yl)vinyl)naphtho
[1,2-*d*]oxazole



(*E*)-2-(2-(benzofuran-2-yl)vinyl)naphtho
[1,2-*d*]oxazole



2-(benzofuran-2-yl)naphtho
[1,2-*d*]oxazole

Results obtained employing steady state shows that these naphthoxazole derivatives have fluorescence quantum yields ranging between 0.02 – 0.8 and a small dependence of the fluorescence spectra on the solvent polarity. However fluorescence (E)-2-(2-(furan-2-yl)vinyl)naphtha [1,2-d]oxazole increases dramatically after irradiation in the presence of singlet molecular oxygen sensitizer. This result indicates that naphthoxazole derivatives including a furyl substituent can be used as very sensitive probes to monitor singlet molecular oxygen in non-polar microenvironments.

Acknowledgements Financial support from FONDECYT (grant 1080410) is gratefully acknowledged.

P48

ESTUDIO TEÓRICO-EXPERIMENTAL DE LAS TRANSICIONES ELECTRÓNICAS DEL COLORANTE *VIOLETA DE METILENO BERNTHSEN*

Carlos A. Glusko[1,2], **Gabriel E. Jara**[3], **Adriana B. Pierini**[3], **D. Mariano A. Vera**[3],
Carlos M. Previtali[1], **Carlos A. Chesta**[1], **Hernán A. Montejano**[1]

[1] Departamento de Química, UNRC, Río Cuarto, Argentina.
[2] Área de Cs. Básicas. Facultad de Agronomía. UNLPam, Santa Rosa, Argentina.
[3] INFIQ -Departamento de Química Orgánica, Facultad de Química, UNC, Argentina.

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

Palabras clave: Fotofísica; Efectos de solvente; Colorantes, TD-DFT

Se presenta un estudio de las propiedades fotofísicas de *Violeta de Metileno Bernthsen* (VMB), colorante sintético neutro de la familia de las fenotiazinas, potencialmente apto para ser empleado como sonda fluorescente y como sensibilizador de diversos procesos inducidos por luz. Tanto los espectros de absorción (de los estados fundamental y triplete) como los de emisión son altamente dependientes de la polaridad y de la naturaleza (prótica o no prótica) del solvente. En solventes apróticos sólo una transición sería responsable de la banda observada, en tanto que en solventes próticos la magnitud de los corrimientos es diferente y aparece una segunda banda. El efecto de solvente sobre los corrimientos de Stokes no puede interpretarse utilizando los modelos solvatocrómicos usuales. A fin de explicar este comportamiento anómalo se realizaron estudios teóricos mediante el uso de métodos mecano-cuánticos de primeros principios (MC) y de dinámica molecular (DM). Se llevaron a cabo estudios de TD-DFT empleando diferentes funcionales, entre ellos PBE0 y B3LYP con bases aug-CC-pVDZ y 6-311+G(2df,p) empleando un modelo de solvente continuo (IEFPCM). Los medios simulados fueron fase gaseosa, heptano, acetonitrilo y metanol. Estos cálculos permitieron asignar las frecuencias de los primeros estados excitados. La transición de menor energía en solventes polares es $\pi-\pi^*$. Los momentos dipolares de los estados fundamentales y primer singlete excitado dependen marcadamente de la polaridad del medio, lo cual podría explicar el comportamiento divergente de los corrientes de Stokes experimentales con los modelos solvatocrómicos. Sin embargo, la aproximación del solvente continuo no explica en su totalidad los resultados experimentales. Por ejemplo, los espectros de absorción muestran un corrimiento significativo al rojo de la primera transición $\pi-\pi^*$ en metanol respecto de acetonitrilo y con desdoblamiento de la banda, mientras que los espectros simulados son similares en ambos solventes. Mediante DM se simuló el solvente discreto metanol caracterizándose puentes hidrógenos persistentes en el tiempo de naturaleza simple y doble, involucrando el oxígeno carbonílico del colorante. Cálculos de MC sobre instantáneas del sistema equilibrado empleando un modelo mixto indicaron un fuerte incremento de la fuerza del oscilador para la segunda transición $\pi - \pi^*$ y de fuertes corrimientos al rojo de ambas transiciones $\pi - \pi^*$, en mejor acuerdo con el experimento. Se racionalizaron los cambios observados mediante el análisis de NBO de las interacciones con moléculas de metanol.

P49

FOTODEGRADAÇÃO DO POLI(METACRILATO DE METILA, PMMA), POLI(METACRILATO DE ETILA, PEMA), POLI(METACRILATO DE BUTILA, PBMA) E POLI(METACRILATO DE HEXILA, PHMA) NA PRESENÇA DE MACROFOTOINICIADORES *MMA-CO-TXA*, *EMA-CO-TXA*, *BMA-CO-TXA* E *HMA-CO-TXA*

Beatriz E. Goi[1], Letícia F. Abdias[2], Carla C.S. Cavalheiro[2], Miguel G. Neumann[2]

[1]Departamento de Física, Química e Biologia, Universidade Estadual Paulista, *UNESP*, Campus de Presidente Prudente, Brasil, Rua Roberto Simonsen, beatriz_goi@fct.unesp.br
[2]Departamento de Físico-Química, Instituto de Química de São Carlos, Universidade de São Paulo, *USP*, São Carlos, Brasil

Palavras chave: fotodegradação, macrofotoiniciadores, tioxantona

O estudo de polimerizações fotoiniciadas por *via* radicalar tem sido tema de inúmeras pesquisas. Recentemente, o desenvolvimento de novos fotoiniciadores incorporados em cadeias poliméricas, denominados de macrofotoiniciadores, está recebendo especial atenção. A natureza macromolecular desses compostos oferece vantagens quando comparados com os correspondentes análogos de baixa massa molar (velocidade de migração menor, melhora na solubilidade e também a possibilidade de desenho da macromolécula). Tioxantonas e seus derivados novamente têm sido foco de interesse devido a suas propriedades de absorção características no UV próximo. Por outro lado, devido a seu procedimento sintético, as tioxantonas, permitem modificações em sua estrutura que podem incluir derivados solúveis em meio aquoso e deslocamento do máximo de sua banda de absorção para o vermelho ou azul dependendo dos substituintes. O objetivo do trabalho é avaliar a fotodegradação dos polímeros PMMA, PEMA, PBMA e PHMA com luz visível na presença dos macrofotosensibilizadores *MMA-co-TXA*, *EMA-co-TXA*, *BMA-co-TXA* e *HMA-co-TXA* (“macrosensibilizadores”)

A Figura 1 ilustra os gráficos obtidos para a degradação dos polímeros PMMA, PEMA, PBMA e PHMA na presença dos fotosensibilizadores macromoleculares *MMA-co-TXA*, *EMA-co-TXA*, *BMA-co-TXA* e *HMA-co-TXA*, respectivamente. Para a determinação da constante de velocidade de degradação (k_d) utilizou-se apenas a parte linear inicial dos gráficos da Figura 1 **A**.

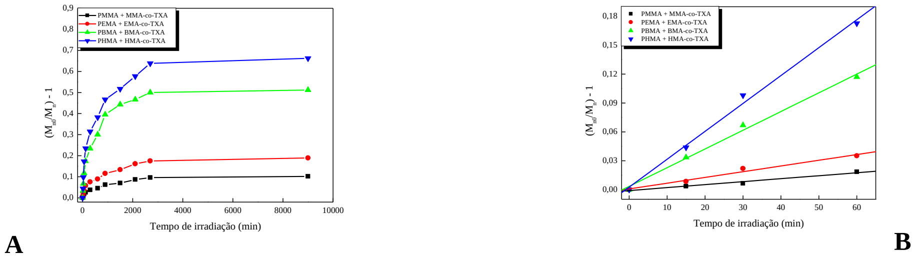


Figura 1. (A) Variação da massa molar numérica média dos polímeros PMMA, PEMA, PBMA, PHMA na presença de TXA em todos os tempos de irradiação. **(B)** Variação da massa molar numérica média dos polímeros PMMA, PEMA, PBMA, PHMA na presença de TXA no intervalo de tempo entre 0 e 60 minutos de irradiação (parte linear inicial).

Pode-se concluir que a constante de velocidade de degradação (k_d) aumenta com o aumento do tamanho do grupo alquila, seguindo a seguinte ordem: PHMA > PBMA > PEMA > PMMA.

P50

MODEL DRUGS RELEASE FROM 2-HYDROXYETHYLMETHACRYLATE / ACRYLAMIDE HYDROGELS SYNTHESIZED BY PHOTOPOLYMERIZATION: INFLUENCE OF THE IONIC CHARACTER OF THE DRUGS.

María Lorena Gómez[a], Roberto J. J. Williams[a], Hernán A. Montejano[b], Carlos M. Previtali[b]

[a]*Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina. E-mail: mlgomez@fi.mdp.edu.ar – williams@fi.mdp.edu.ar*
[b]*Department of Chemistry, University of Río Cuarto and National Research Council (CONICET), Campus Universitario, 5800 Río Cuarto, Argentina. E-mail: hmontejano@exa.unrc.edu.ar – cprevitali@exa.unrc.edu.ar*

Keywords: Photopolymerization; Drug release; Hydrogels.

In this work we report the synthesis of hydrogels employing visible-light photopolymerization. A silsesquioxane functionalized with methacrylate and amine groups (SFMA) was employed as crosslinker/co-initiator to obtain hydrogels, based on 2-hydroxyethylmethacrylate (HEMA) and acrylamide (AAm); safranine O (Saf) was employed as sensitizer. The source of light was provided by a photoreactor with eighth LEDs of 530 nm, hydrogels with a high swelling capability were synthesized.

These hydrogels were loaded with different model drugs; the influence of the ionic character of a specific drug on its release rate from the hydrogel was analyzed. The following ionic or uncharged dyes were employed to mimic drugs: acridine orange (AO) as a neutral drug, safranine O (Saf) as a cationic drug, and resorufin (Rf) as an anionic drug. The release rates of the dyes were investigated by UV-Vis spectroscopy.

A very high amount of the neutral dye could be loaded; the proportion was less but still significant for the cationic dye and almost negligible for the anionic dye. This means that the poly(HEMA-*co*-AAm) hydrogel is not suitable for the loading with anionic drugs (assuming that the behavior shown by the particular anionic dye used in this study can be extrapolated to other anionic drug). The significant loading observed for the cationic dye implies the existence of specific interactions between the cation and functional groups of the hydrogel. While the release rate of AO and Rf was relatively fast and followed a Fickian behavior, the release rate of Saf was slow and exhibited a non-Fickian behavior giving extra evidence of the presence of specific interactions with the hydrogel. Therefore, poly(HEMA-*co*-AAm) hydrogels are suitable for the high loading and fast release of neutral drugs and the intermediate loading and slow release of cationic drugs.

Converting the amide into carboxylate groups by hydrolysis of the hydrogel at pH = 13, produced a significant increase of the loading capacity of the cationic dye and a significant decrease of its release rate. This was explained by the higher specific interactions of the cationic dye with carboxylate/carboxylic acid groups compared with amide groups. In conclusion, tuning the ionic character of a drug and the conversion of amide groups into carboxylate groups enables to control the loading capacity and the release rate from poly(HEMA-*co*-AAm) hydrogels used in drug-delivery applications.

P51

ESTUDIO CINÉTICO DE LA REACCIÓN $CCl_2 + O_2$ POR MEDIO DE FLUORESCENCIA INDUCIDA POR LASER

Nicolás Gómez*, Mariana Freytes*†, Jorge Codnia*, Francisco Manzano*, Laura Azcárate*†

* CEILAP (CITEDEF-CONICET), Villa Martelli, Buenos Aires, Argentina, J. B. de La Salle 4397. e-mail : ndgomez@live.com.ar mfreytes@citefa.gov.ar, Jcodnia@citefa.gov.ar, fmanzano@citefa.gov.ar, lazcárate@citefa.gov.ar.
† Carrera del investigador CONICET.

Palabras clave: LIF, diclorocarbeno, DMFIR.

En el presente trabajo se estudió la cinética de reacción del radical diclorocarbeno, CCl_2, en presencia de O_2 y Ar. Para ello se implementó la técnica de Fluorescencia Inducida por Láser (LIF) en una facilidad de disociación multifotónica IR (DMFIR).

Los radicales CCl_2 se generaron a partir de la DMFIR de $CDCl_3$ con un láser de CO_2 TEA pulsado a 1Hz y sintonizado en la línea 10P(48), resonante con el modo vibracional ν_4 de la molécula de $CDCl_3$. Posteriormente estos radicales se excitaron al nivel electrónico A^1B_1 con pulsos de un láser de colorante bombeado por un láser de Nd:YAG. La señal de fluorescencia emitida por los radicales diclorocarbeno al decaer al nivel fundamental fue detectada mediante un fotomultiplicador. El seguimiento temporal de las concentraciones de los radicales CCl_2 se realizó retardando el pulso del láser de colorante respecto del pulso del láser TEA de CO_2.

El análisis de la evolución temporal de las señales de fluorescencia de las mezclas con Ar permitió caracterizar la difusión y la reacción de recombinación entre radicales CCl_2. A su vez, mediante un análisis similar de las señales provenientes de las mezclas con O_2 se determinó la constante de velocidad de reacción de los radicales CCl_2 con O_2.

La reacción de los radicales CCl_2 con O_2 conduce a la formación de oxígeno atómico, el cual, a su vez, inicia un ciclo catalítico de disociación de $CDCl_3$. Se llevó a cabo el estudio de las señales de fluorescencia de los radicales CCl_2 generados a partir de la DMFIR de $CDCl_3$ en mezclas con $CHCl_3$ y con O_2 a fin de evidenciar, en la competencia entre las dos especies isotópicas, el mecanismo de disociación subsiguiente a la DMFIR.

P52

DETERMINACIÓN DEL EFECTO FOTOPROTECTOR DE DERIVADOS DE BOLDINA

Patricio González S.[1], María E. Hidalgo L.[2], Eduardo Sobarzo-Sánchez[3]
y J. De la Fuente, [4]

[1]Facultad de Farmacia, Universidad de Valparaíso, Valparaíso, Chile, e-mail: patricio.miguelgonzalez@gmail.com
[2] Facultad de Ciencias, Universidad de Valparaíso, Valparaíso, Chile. e-mail: maria.hidalgo@uv.cl
[3] Facultad de Química, Universidad de Santiago de Compostela, España, e-mail: esobarzo@usc.es
[4] Facultad de Ciencias Químicas y Farmacéuticas, Santiago de Chile, Chile, e-mail: jrfuente@ciq.uchile.cl

Palabras clave: Radiación UV, boldina, fotoprotector.

El incremento de la luz UV que alcanza la superficie terrestre debido a la disminución de la capa de ozono y la mayor exposición de las personas a las radiaciones solares o lámparas UV, por la moda que impone el bronceado, ha llevado a un aumento de enfermedades como cáncer de piel, lupus eritematoso, xerodema pigmentosa y que han conducido, en la actualidad, al estudio de compuestos naturales con gran capacidad fotoprotectora.

La boldina ((S)-1,10-dimetoxiaporfina-2,9-diol) alcaloide presente en corteza y hojas del Peumus Boldus Molina, muestra una gran capacidad filtrante y protectora de radiación en especial en el rango UV-B, lo cual se debe a la gran estabilidad que confiere la estructura aporfínica y fenólica a la molécula.

Se determinó la capacidad fotoprotectora de 4 derivados de boldina: nitroso boldina, amino boldina, oxazol boldina y feniloxazinona boldina, a través de la determinación del factor de protección solar por medio de células de fibroblastos y por el método de transmitancia, además de determinar la capacidad fototóxica en modelos de glóbulo rojo y Artemia salina, con el objeto de aportar evidencia de sustancias fotoprotectoras naturales, así como de sus futuras aplicaciones.

En las soluciones sin irradiar, los FPS de los derivados de boldina clorhidrato son mayores que el FPS de boldina clorhidrato, siendo el más alto, el de amino boldina clorhidrato, indicando que los grupos sustituyentes de los derivados aumentan la capacidad fotoprotectora lo que se manifiesta en un aumento en la sobrevida de células de fibroblastos, destacando oxazol boldina clorhidrato y feniloxazinona boldina clorhidrato.

En el modelo de glóbulo rojo, las soluciones de boldina clorhidrato y sus cuatro derivados en forma de sal, no producen hemólisis en oscuridad. Las soluciones, preirradiadas de amino boldina clorhidrato, nitroso boldina clorhidrato y oxazol boldina clorhidrato provocaron un 20% de hemólisis, y feniloxazinona boldina y boldina clorhidrato alrededor del 10%. En ensayos de fotohemólisis, feniloxazinona boldina clorhidrato, nitroso boldina clorhidrato y oxazol boldina clorhidrato produjeron un 10 % de hemólisis; en tanto que amino boldina clorhidrato y boldina clorhidrato alrededor del 5%.

En el modelo de Artemia salina, boldina clorhidrato y sus cuatro derivados en forma de sal, muestran una Dosis Letal 50 (DL50) promedio de 800 ppm, la fotoletalidad fue en promedio de 500 ppm y en soluciones preirradiadas fue de 350 ppm .

P53

EFECTO DE FOTOSENSIBILIZANTES NATURALES SOBRE EL METABOLISMO OXIDATIVO DE CELULAS VERO

Grasso Sergio[1], Konigheim Brenda[2], Aguilar Javier[2], Cabrera José[1] y Núñez Montoya Susana[1].

[1] Farmacognosia, Fac. Cs.Qcas., Univ. Nac. Córdoba, IMBIV-CONICET. Cba., Arg.
[3] Instituto Virología, Fac. Cs. Médicas, UNC. Ciudad Universitaria (5016) Córdoba, Argentina.
E-mail: sgrasso@fcq.unc.edu.ar

Palabras claves: antraquinonas, *Heterophyllaea pustulata*, Fotosensibilizantes

A partir de las partes aéreas de una especie argentina, *Heterophyllaea pustulata* Hook. f. (Rubiáceas), aislamos antraquinonas (AQs) con propiedades fotosensibilizantes: soranjidiol (**1**), rubiadina (**2**), 1-metil éter de soranjidiol (**3**), 1-metil éter de rubiadina (**4**), damnacantal (**5**), damnacantol (**6**), heterofilina (**7**), pustulina (**8**) y 5,5´-bisoranjidiol (**9**) [1-4]. Asimismo, demostramos que estas AQs inhiben el virus del herpes simple tipo I (VHS-I) *in vitro*, efecto determinado sobre células Vero mediante el ensayo de reducción de unidades formadoras de placas (ufp) bajo agarosa. A su vez, establecimos que esta inhibición viral es incrementada por acción de la luz para seis de estas AQs (**1**, **2**, **3**, **6**, **7** y **8**) [5]. En este trabajo evaluamos la actividad de las nueve AQs aisladas de *H pustulata*, sobre el metabolismo oxidativo de las células Vero (producción de $O_2^{\cdot -}$ *in vitro*), bajo condiciones de oscuridad e irradiación, a fin de descartar un efecto fototóxico sobre estas células huésped.

Las AQs se probaron por duplicado a una concentración que asegura el 90% de la viabilidad celular (10 µg/ml), determinada por el ensayo de captación de rojo neutro. Cada AQ se disolvió en PBS-DMSO (1%). La producción de O_2^{-} se evaluó mediante el ensayo de NBT (Nitroblue Tetrazolium), el cual se reduce a azul de formazán por acción de esta especie reactiva del oxígeno, producida por las células Vero (3×10^6 cél/ml) en presencia de un agente oxidante (AQs). Se incluyeron controles celulares por duplicado. Este ensayo biológico indirecto se realizó bajo condiciones de oscuridad y radiación UV (RUV = 380-480 nm) durante 15 min a T° ambiente. Posteriormente, todas las muestras y controles se incubaron a 37 °C durante 60 min. Se midió la absorbancia del azul de formazán generado en el interior de las células Vero por espectrofotometría UV-V (λ= 575 nm). El incremento en la producción de $O_2^{\cdot -}$ respecto al basal (control celular, 100 %) se expresó en porcentaje.

Los resultados obtenidos establecen que sólo dos de estas AQs, 1-metil éter de soranjidiol (3) y pustulina (8), no estimulan el metabolismo oxidativo de las células Vero en oscuridad, el cual tampoco es afectado por acción de la luz a la concentración ensayada. Esto implica que estas AQs, a 10 µg/ml y bajo RUV, muestran un importante incremento en la inhibición del VHS-I (> 90%), sin generar estrés oxidativo en la célula huésped (Vero).

Bibliografía:
1. SC Núñez Montoya, AM Agnese, C Pérez, IN Tiraboschi, JL Cabrera. (2003) Phytomedicine 10, 569-574.
2. SC Núñez Montoya, AM Agnese, JL Cabrera. (2006) J. Nat. Prod. 69, 801-803.
3. SC Núñez, LR Comini, M Sarmiento, C Becerra, I Albesa, G Argüello, JL Cabrera. (2005) J. Photochem. Photobiol. B 78, 77-83.
4. LR Comini, SC Núñez Montoya, M Sarmiento, JL Cabrera, Gustavo A Argüello. (2007) J. Photochem. Photobiol. A 188, 185-191.
5. SC Núñez Montoya, JJ Aguilar, BS Konigheim, MS Contigiani, JL Cabrera. XVI Congreso Italo-Latinoamericano de Etnomedicina (SILAE). La Plata, 04-08/09/2007.

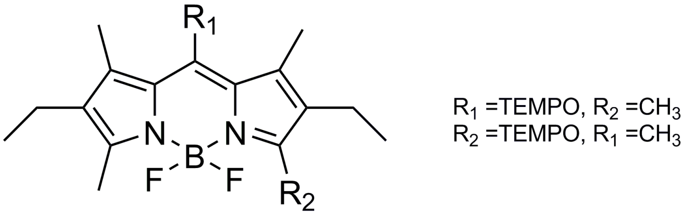
P54

Interaction of BODIPY nitroxide probes with human serum albumin

Camila Gutiérrez,[1] Marta Liras,[2] Soledad Ureta,[1] Alexis Aspée[1]
1 Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile.
2 Instituto de Química Orgánica, ISIC, Madrid, España.
email: alexis.aspee@usach.cl

Palabras clave: BODIPY, nitroxide probes, antioxidant, human serum albumin.

BODIPY dyes have been widely employed in imaging applications for biological systems due to their absorption and fluorescent emission at long wavelengths, high fluorescent quantum yields and high stability.[1]



In the present work we evaluate the photophysical properties of different new synthesized nitroxide-BODIPY dyes and their interaction with human serum albumin. Time resolve fluorescent measurements showed an efficient intramolecular quenching of the BODIPY fluorescence by the nitroxide moiety in these probes. In addition, fast recovery of the fluorescence in time is observed when these dyes are incubated with ascorbic acid or Trolox, in agreement with a reduction of the nitroxide unit by electron and/or hydrogen transfer from these antioxidants. The efficient fluorescent quenching of the Trp 214 in HSA by BODIPY nitroxide probes allowed establishing a high association constant with HSA in site I binding site. The incorporation of the nitroxide probes in HSA binding sites is discussed in terms of the accessibility of antioxidants ascorbic acid and Trolox to reduce the nitroxides.[2]

Acknowledgments: Financial support from FONDECYT 1085177.

1. Liras, M., Prieto, J. B., Pintado-Sierra, M., López Arbeola, F., García-Moreno, I., Costela, A., Infantes, L., Sastre, R., Amat-Guerri, F. *Org. Lett.* 2007, **9**, 4183.
2. Aspée, A., Orrego, A., Alarcón, E., López-Alarcón, C., Poblete, H., González-Nilo, D. *Bioorg. Med. Chem. Lett.*, 2009, **19**, 6382.

P55

ESTABILIDAD DE ÁCIDO ASCÓRBICO EN PRESENCIA DE RIBOFLAVINA Y LUZ VISIBLE

Ernesto Haggi[1], Néstor Blasich[1], Sandra Miskoski[2] y Norman A. García[2]

[1] Unidad Académica Río Gallegos. Univ. Nac. de la Patagonia Austral. 9400 Río Gallegos. Argentina
[2] Departamento de Química. Univ. Nac. de Río Cuarto. 5800 Río Cuarto. Argentina

Palabras Clave: Ácido Ascórbico; Fotosensibilización; Riboflavina

El efecto fotoprotector antioxidante del ácido ascórbico (Asc) frente a diferentes compuestos es ampliamente conocido y algunos aspectos del mismo siguen siendo estudiados en la actualidad. En especial, cuando se lo relaciona con fotosensibilizadores naturales como Riboflavina (Rf, Vitamina B2), en presencia de luz visible y de relevantes sustratos biológicos oxidables como los aminoácidos[1,2]. No obstante son muy pocos los casos en que la investigación se centra sobre la fotoestablidad del Asc, un detalle que debe considerarse vital a la hora de establecer la perdurabilidad del compuesto como fotoprotector en un dado medioambiente. Paralelamente, la propia acción del Asc –en base a sus propiedades como buen electrodonante– puede generar, en presencia de ciertos sensibilizadores, y en el caso de Rf por interacción con sus estados electrónicamente excitados, diversas especies reactivas de oxígeno (ROS). Aunque éstas puedan ser interceptadas por el mismo Asc, generalmente producen degradación del ácido y aportan al medio justamente ROS que pueden actuar frente a otros sustratos supuestamente fotoprotegidos por el Asc.

En este trabajo presentamos un estudio cinético y mecanístico en solución acuosa, acerca del efecto fotogenerador de las especies ion superóxido, peróxido de hidrógeno y radical OH por el sistema Rf-Asc-oxígeno-luz visible, su acción sobre el Asc. y un análisis detallado sobre las propiedades desactivantes de oxígeno molecular singlete por el Asc, en función del pH.

---

[1] J. García and E. Silva. Int. Nutr. Biochem., 8, 341-345 (1997)

[2] R. R. Yattella and D. B. Min., Food Chem., 118, 35-41 (2010)

P56

COMPLEXO BINUCLEAR DE Ru(II) E Mn(I) PARA PRODUÇÃO DE ENERGIA

Simone D. Inglez*, Yuri Dezotti*, Guilherme Chinini*, Antonio C. Tedesco#, Rose M. Carlos*

*Departamento de Química, Universidade Federal de São Carlos, São Carlos, Brasil.
#Departamento de Química, Faculdade de Ciências e Letras de Ribeirão Preto-USP, Ribeirão Preto, Brasil
simoneinglez@ufscar.br

Palavras Chaves: Fotossíntese Artificial, Transferência de Elétrons, Complexos Binucleares

Pesquisas vêm sendo realizadas para os métodos de conversão de energia solar em energia elétrica ou química. Esses processos podem ser considerados modelos biomiméticos da fotossíntese porque usam a energia transferida por um fotossensibilizador para gerar um estado excitado com separação de cargas e neste estado excitado transferem a energia para uma molécula receptora. Neste sentido nós apresentamos a síntese e as propriedades fotofísicas de um complexo binuclear de Ru(II) e Mn(I) coordenados pelo ligante ponte 4,4'-bipiridina. Os complexos mononucleares de Ru(II) e Mn(I) também foram sintetizados para comparação. O complexo binuclear que está sendo estudado para participar de processos de tranferência de elétrons é do tipo $[Ru^{II}(phen)_2(4,4'\text{-}bpy)_2\text{-}Mn^{I}(CO)_3(Im)]$. No complexo de Mn(I), a unidade $[Mn(CO)_3(4,4'\text{-}bpy)_2(Im)]^+$, atuará como doador de elétrons para a espécie a ser reduzida e o complexo de Ru(II) com a unidade $[Ru(phen)_2(4,4'\text{-}bpy)_2)]^{2+}$ atuará como fotossensibilizador. As propriedades espectroscópicas, fotoquímicas e fotofísicas para cada unidade e para o complexo binuclear são avaliadas individualmente e a viabilidade do processo de transferência de elétrons também foi investigada. O espectro de absorção eletrônica do complexo mononuclear e binuclear de Ru(II) são dominados por uma banda na região do visível (420 nm) que são atribuídas como transições de transferência de carga (MLCT) de Ru → phen e Ru → 4,4'-bpy, e por transições intensas de alta energia (225 e 265 nm), devido as transições centradas nos ligantes (LC) envolvendo ligantes phen e 4,4'-bpy. Os complexos apresentam emissão no comprimento de onda na região de 600 nm, característicos de complexos polipiridínicos de Ru(II). O cálculo do orbital molecular (DFT) dos complexos foram realizados e o valor de *gap* encontrado para o complexo mononuclear de rutênio foi de 3,48 eV e para o complexo binuclear de rutênio foi de 2,99 eV, este decréscimo foi obsevado no orbital LUMO quando o complexo de Ru(II) é coordenado ao Mn(I), o orbital LUMO do binuclear muda do ligante fenantrolina para o 4,4'-bipiridina, devido ao efeito retirador de elétron do complexo de Mn(I). Na presença de compostos receptores de elétrons externos como cloreto de N,N-dimetil-4,4'-bipiridina (MV^{2+}), o complexo binuclear depois de ser excitado com um laser à 355 nm conduziu a uma transferência de elétrons intermolecular do estado excitado de Ru(II) para MV^{2+}, com a formação de $MV^{+\bullet}$ e Ru(III). O aparecimento de Ru(II) e o desaparecimento de $MV^{+\bullet}$ foram monitorados à 420 e 610 nm, respectivamente. Este resultado mostra que a transferência de elétrons do Mn(I) coordenado para o fotossensitizador oxidado é possível, abrindo o caminho para a etapa de transferência de elétrons na fotossíntese artificial.

P57

COMPARATIVE STUDY OF OPTICAL SIGNALS FROM FLOWERS RELEVANT IN BIOCOMMUNICATION

Analia Iriel and M. Gabriela Lagorio

Departamento de Química Inorgánica, Analítica y Química Física/ INQUIMAE. FCEyN, UBA. Buenos Aires, Argentina. Ciudad Universitaria, Pabellón 2, 1er piso.
e-mail: airiel@qi.fcen.uba.ar and mgl@qi.fcen.uba.ar

Key words: photoreceptor, fluorescence quantum yield, reflectance

The light that emerges from the flowers is an important signal used for biological systems to communicate with pollinator agents. In general, the spectral composition of the emerging light is due to reflected radiation. However, in some cases, phenolic compounds and dyes present in petals may contribute with fluorescence emission.

The aim of this study was to evaluate the relative importance of fluorescence compared to reflectance for biocommunication. Intact petals from *Portulaca grandiflora, Lanpranthus productus, Bellis Perennis, Citrus anarantium, Antirrhinium majus* among others were studied in detail.

In a preliminary study we adapted a methodology described in literature for calculating the fluorescence quantum yield in intact petals.[1] Following this procedure we were able to estimate quantitatively the fluorescence contribution for the studied species. In addition, reflectance spectra of the flowers were recorded. These results were evaluated in combination with the color vision system of the pollinators, the illumination source and the background contrast.

In all cases, the fluorescence emission that resulted was negligible compared to the light reflected by the petals, so that it was concluded that only reflectance signals should be relevant in biosignal communication with pollinators. In addition, a quantitative estimation of the relative amount of photons absorbed by the eye photoreceptors was achieved. Quantum catches were calculated for humans, for honeybees and for a species of bird.

This research involves a quantitative description of the light emerging from the flowers that could complement behavioural experiments of pollinators.

[1] A. Iriel, M.G. Lagorio, Biospectroscopy of Rhododendron indicum flowers. Non-destructive assessment of anthocyanins in petals using a reflectance-based method, Photochem. Photobiol. Sci., 2009, 8, 337

P58

CHEMICAL SYNTHESIS WITH LIGHT IRRADIATION OF NANOCRYSTALS OF CdTe

Patricio Jara[a], **Igor Osorio-Román**[ab], **Ricardo Aroca**[c], **Victoria Ortega**[a] **and Victor Vargas**[a]

[a] Department of Chemistry, Faculty of Science, Universidad de Chile, Las Palmeras 3425, Santiago, Chile. email: gjara@uchile.cl
[b] Department of Environmental Chemistry, Faculty of Chemistry and Biology, Universidad de Santiago de Chile, Av. B. O'Higgins 3363, Santiago, Chile.
[c] Department of Chemistry and Biochemistry, Faculty of Sciences, University of Windsor, 273-1 Essex Hall, 401 Sunset Avenue, Windsor, Canada.

Keywords: synthesis; light; nanocrystals

Semiconductor nanocrystals are light-emitting particles in the nanometer scale. Researchers intensely have studied these particles the last decade, as these have many applications. One of the disadvantages of these nanoparticles is its fabrication, since the high temperature required for synthesis can be problematic for its production. For this reason, our goal is to develop a new methodology for the synthesis of semiconductor nanocrystals with light irradiation. In literature there are a few publications [1-3] related to the subject of synthesis with light or photosynthesis. Truthful information on the condition of formation of the nanoparticles due to the effect of light is scarce. In this sense, our bibliographical revision shows that the light could control the formation of nanoparticles by affecting the small clusters of atoms, called seed [1-3]. The seeds are the base of formation of nanoparticles, because they determine the size and shape of the final product. To achieve this goal, we intend to carry out the photosynthesis with polychromatic light of nanocrystals of CdTe. The characterization of the semiconductor nanocrystal will be performed using UV-visible spectra, fluorescence spectra, lifetime of the excited state, scanning electron microscope (SEM), and studies of the composition of the unit cell with X-ray diffraction (XRD).

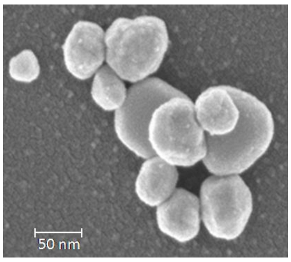


Figure 1. SEM of nanocrystals of CdTe fabricated with irradiation of light.

References

1. J. Zeng, C. Liu, J. Huang, X. Wang, S. Zhang, G. Li and J. Hou, *Nano Lett.*, 2008, **8**, 1318-1322.
2. N. B. Egorov, L. P. Eremin, A. M. Larionov, V. F. Usov and I. P. Fiterera, *Russ. Chem. Bull.*, 2008, **57**, 2483-2486.
3. A. E. Raevskaya, A. L. Stroyuk and S. Y. Kuchmii, *Theor. Exp. Chem.*, 2005, **41**, 181-186.

P59

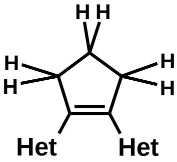
PHOTOCHROMIC COMPOUNDS FOR THREE-DIMENSIONAL OPTICAL MEMORY

Mikhail Krayushkin, Vladimir Yarovenko, Valerik Shirinyan, Alexey Shimkin, Sergey Luiksaar, Marina Kalik, Vasily Migulin, #Valery Barachevsky

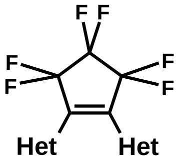
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47, Leninsky prosp., 119991, Moscow, Russia, mkray@ioc.ac.ru .
#Institution of the Russian Academy of Sciences, Photochemistry Center of RAS, Moscow,
Russia, 119421, 7a-1, Novatorov Str., barva@photonics.ru

Key Words: photochromes, optical memory

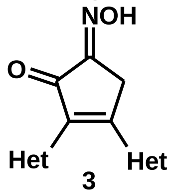
Methods for preparation of dihetarylethenes 1-4 and fulgimides 5-7 were developed.



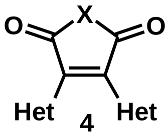
1



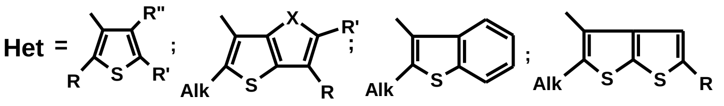
2



3

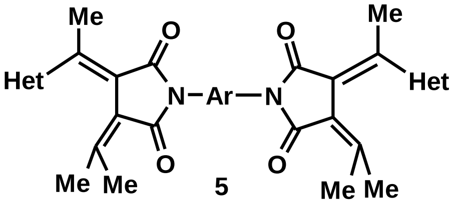


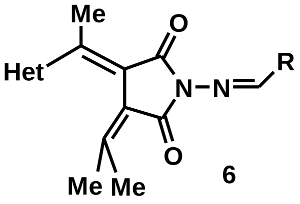
X = O, NR

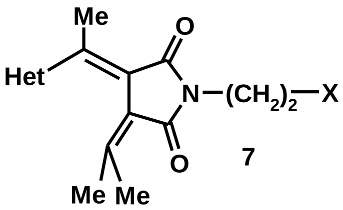


X = S, NAlk

R,R',R" = H,Alk,Ar,Hal,CHO,COOH,Het

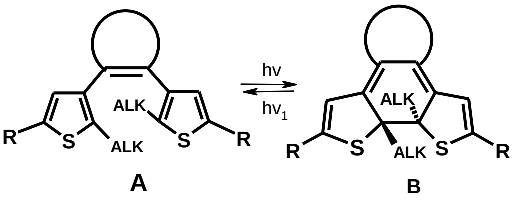


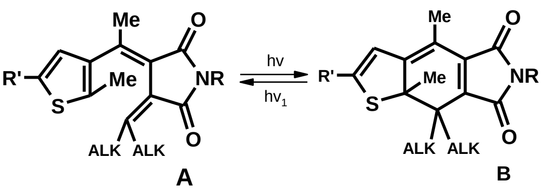




X = OH, SH, NAlk

It was shown that all products are photochromes and possess thermal irreversibility (open forms A convert into cyclised forms B and conversely at irradiation only).





Many substances have rather high fatigue resistance. Photochemical studies of the compounds show they to be candidates for using as light-sensitive components of recording media for three-dimensional optical memory of the operative (rewritable) type.

P60

FOTOGERAÇÃO DE HIDROGÊNIO A PARTIR DA DISOCIAÇÃO DA ÁGUA UTILIZANDO NANOTUBOS DE TiO_2 E ALCOÓIS COMO COMPOSTOS DE SACRIFICIO

Mariana Languer*, Matheus D. Pierozan#, Rodrigo R. Corsetti#, Pedro Migowski*, Adriano F. Feil#, Jairton Dupont*, Sérgio R. Teixeira# e Daniel E. Weibel*

* Instituto de Química, Universidade Federal de Rio Grande do Sul, Porto Alegre, Brasil,
danielw@iq.,ufrgs.br
Instituto de Física, Universidade Federal de Rio Grande do Sul, Porto Alegre, Brasil,
durao@if.ufrgs.br

Palabras chave: Hidrogênio, Fotocatalise, Nanotubos

Desde o século passado os combustíveis fósseis são fontes de energias muito populares sendo seus principais problemas: poluição ambiental e fontes não renováveis. Toda essa problemática não existe em fontes de energia baseadas em sistemas que consomem H_2. Os processos fotocatalíticos sobre superfícies de semicondutores têm chamado muito a atenção de pesquisadores desde sua descoberta [1]. Esses mecanismos são considerados de alto potencial de aplicação para a geração renovável de hidrogênio devido principalmente à compatibilidade ambiental e baixos custos. O aumento recente na pesquisa na área de fotogeração de H_2 é devido à utilização de novos fotocatalizadores nanoestruturados.

Na seguinte contribuição serão apresentados os resultados obtidos na fotogeração de hidrogênio utilizando nanotubos (NTs) de TiO_2 preparados por anodização eletroquímica de substratos de Ti. As reações fotocatalíticas foram realizadas num reator fotoquímico fechado construído de teflon especialmente para esse fim. A fonte de excitação utilizada foi uma lâmpada de Xe/Hg de 150 W de potencia. Eficiências quânticas de geração de hidrogênio (ϕ_{H2}) foram determinadas pelo método de actinometria química utilizando o Ferrioxalato de potássio como actinómetro. Soluções aquosas de diferentes compostos orgânicos principalmente alcoóis foram irradiadas com agitação permanente e a evolução de hidrogênio foi medida por cromatografia gasosa. Os nanotubos de TiO_2 foram caracterizados por difração de Raios-X, SEM e UV-difuso.

A taxa de fotogeração de H_2 obtida com diferentes NTs mostrou-se muito estável e com um aumento proporcional à concentração de álcool (metanol, etanol, glicerol, etc.) por períodos ≥ 24 horas de irradiação continua. Comparando a produção de hidrogênio em água pura com, por exemplo, a mistura Metanol/Água (V/V) de 22,22 %, a taxa de geração de hidrogênio foi ~ 50 vezes menor em água pura. A ϕ_{H2} utilizando uma solução de 11,11 % de Metanol/Água (V/V) a 365 nm foi de ~ 1 % . Nanotubos preparados com 100 % da fase anastase apresentaram uma produção de H_2 significativamente maior que quando está presente a fase rutila ou uma mistura de ambas. Os compostos orgânicos em água atuam como doadores de elétrons neutralizando as lacunas, diminuindo a eficiência da recombinação elétron-lacuna e em conseqüência aumentando a eficiência na geração de H_2.

[1] Fujishima.A and K. Honda, Nature 238 (1972) 37

P61

INACTIVACIÓN DE LA TOXINA HEMOLÍTICA *STICHOLYSIN I* (St1) POR OXÍGENO SINGULETE

Luis León, Eduardo Lissi y Elsa Abuin
Facultad de Química y Biología, Universidad de Santiago de Chile
L León <ll.mquimico@gmail.com>

Palabras clave: oxígeno singulete, toxinas, oxidación

St I es un miembro de una familia de toxinas altamente hemolíticas aisladas de la anémona *Stichodactyla helianthus*, presente en el Mar Caribe. La actividad hemolítica está asociada a su capacidad para formar poros toroidales en membranas, con el consiguiente shock osmótico conducente a la ruptura celular. Esta capacidad de formar poros se observa también en liposomas, en particular en sistemas que contienen esfingomielina.

La actividad hemolítica de St I depende de la capacidad de organización de la toxina, la que es muy sensible a cambios en su estructura primaria y/o secundaria. Estos cambios pueden ser ocasionados por especies reactivas del oxígeno, tales como radicales peroxilo, hipoclorito y peroxinitrito. El presente trabajo tiene por objetivos:

i) establecer la eficiencia del oxígeno singlete en la inactivación de la toxina; y
ii) establecer el grado de correlación que existe entre la pérdida de actividad hemolítica y la capacidad de formar poros en sistemas modelos.

Los resultados obtenidos permiten concluir que el oxígeno singlete (generado en la irradiación de Rosa de Bengala) es eficiente en la inactivación de la toxina, y que la pérdida de la capacidad para formar poros en sistemas modelos correlaciona estrechamente con la actividad hemolítica.

Los autores agradecen a Fondecyt (Proyectos No. 1070285 y 1095032) el financiamiento de este trabajo

P62

TOKYO GREEN ON CELLULOSE: FLUORESCENCE QUANTUM YIELD AND ENERGY TRANSFER TO A NON-FLUORESCENT ACCEPTOR

Sergio Lopez,* **Luis Crovetto,**[#] **Eva M. Talavera,**[#] **Enrique San Román***

* INQUIMAE / DQIAyQF, Facultad de Ciencias Exactas y Naturales, Universidad de
Buenos Aires, Ciudad Universitaria, Pab. II, C1428EHA Buenos Aires, Argentina,
sgl@qi.fcen.uba.ar
[#] Departamento de Química Física. Campus de Cartuja. Universidad de Granada. Granada
18071, España

Keywords: fluorescent dyes, light scattering solids, energy transfer

Tokyo Green II (TGII, 9-[1-(2-methyl-4-methoxyphenyl)]-6-hydroxy-3H-xanthen-3-one) is a recently developed fluorescein derivative with $pK_a = 6.2$, whose fluorescence quantum yield and lifetime are high in basic solutions ($\Phi = 0.84$, $\tau = 3.7$ ns) and very low in acid media ($\Phi = 0.01$, $\tau = 0.20$ ns).[1,2] Due to this pH-dependence TGII is a promising on-off fluorescent probe. We report here the main photophysical parameters of TGII adsorbed on microcrystalline cellulose. In addition, we characterize the same dye as energy donor to Dabcyl (DB), a non-fluorescent dye, on the same support.

TGII was adsorbed from ethanol at 2×10^{-8} to 2×10^{-6} mol g^{-1}. Remission function spectra resemble the absorption spectrum of the acidic TGII specie in solution. As the shape of the remission function spectrum does not depend on dye loading and its amplitude grows linearly with concentration, aggregation can be disregarded up to 8×10^{-7} mol g^{-1}. Emission spectra are independent of the excitation wavelength and match the spectrum of the acidic (neutral) form. However, the observed fluorescence quantum yield, obtained against adsorbed rhodamine 6G as the reference, is calculated as $\Phi_{obs} = 0.26 \pm 0.1$. Once corrected for inner filter effects,[3] a constant true fluorescence quantum yield, $\Phi = 0.31 \pm 0.1$, is obtained up to 8×10^{-7} mol g^{-1}. The distribution lifetimes on the cellulose surface, explored by fluorescence lifetime imaging microscopy (FLIM), peaks around 3.6 ns.

Mixed TGII-DB samples were prepared in two steps: 1) TGII was adsorbed from ethanol at 1×10^{-7} mol g^{-1} and 2) DB was adsorbed from ethanol at 8×10^{-8} to 3×10^{-6} mol g^{-1}. No evidence of DB aggregation is found in the whole range. Non-radiative energy transfer efficiencies, calculated by means of a previously developed model,[4] are as high as 0.9. Fluorescence decays become shorter and non-exponential as the DB concentration increases, suggesting a Förster type energy transfer mechanism.

The origin of the high Φ and τ values found for the apparently acidic form is analyzed in terms of the dye structure and the interaction with the cellulose surface.

---

[1] Y. Urano, M. Kamiya, K. Kanda, T. Ueno, K. Hirose, T. Pagano. *J. Am. Chem. Soc.* 127 (**2005**) 4888.
[2] J. M. Paredes, L. Crovetto, R. Rios, A. Orte, J. M. Alvarez-Pez, E. M. Talavera, *PCCP* 11 (**2009**) 5400
[3] M. G. Lagorio, L. E. Dicelio, M. I. Litter, E. San Román. *J. Chem. Soc. Faraday Trans*. 94 (**1998**) 419.
[4] S. G. López, G. Worringer, H. B. Rodríguez, E. San Román. *PCCP*, submitted.

P63

LIPOSOMES, CARRIERS FOR *TETRAKIS*-(1-ADAMANTYL SULFANYL) PHTHALOCYANINATO ZINC (II)

Noelia López Zeballos[a,b], María C. García Vior [a,b], Josefina Awruch[b], Lelia E. Dicelio[a].

[a]INQUIMAE/ Departamento de Química Inorgánica, Analítica y Química Física. Facultad de Ciencias Exactas y Naturales, UBA, Pabellón II, C1428EHA, Buenos Aires. Argentina
[b]Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, UBA, Junín 926, 1113 Buenos Aires, Argentina
E-mail: led@qi.fcen.uba.ar

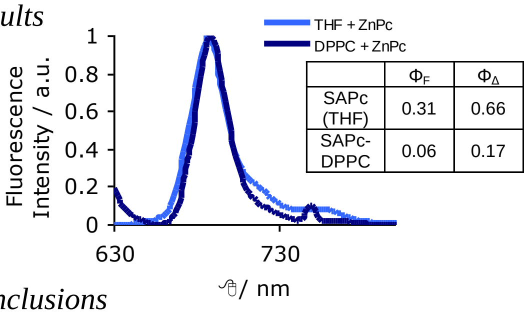
Key Words: liposomes, phthalocyanines, photodynamic therapy.

Zinc(II)phthalocyanine (ZnPc) is one of the so-called second generation agents for photodynamic therapy (PDT), a typical treatment for neoplastic and non-neoplastic diseases. It is a challenge to investigate the effect of liposome carriers on the affinity of a light-sensitive compound for bacterial cells and also on the efficacy of photo-induced bacterial killing. PDT is based on the appropriate combination of oxygen, light and a photosensitizer, which becomes excited and mediates the production of cytotoxic reactive oxygen species. The use of vesicles in drug formulations is based on the observation that the affinities of photosensitizer for neoplastic tissues increases when the degree of hydrophobicity increases, while their selective distribution is improved when they are incorporated to amphiphilic systems. Another advantage of the inclusion of cholesterol in the liposome formulation is that it enhances their mechanical stability, avoiding structural disintegration in blood.

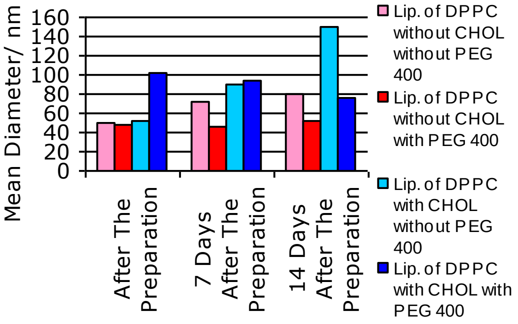
Aim of this study

Incorporation of a lipophilic ZnPc to different formulations of liposomes in order to evaluate the photophysical properties, as well as their size and stability during a time-period.

Results



	Φ_F	Φ_Δ
SAPc (THF)	0.31	0.66
SAPc-DPPC	0.06	0.17



Conclusions

A hydrophobic ZnPc was synthesized and successfully incorporated in DPPC liposomes. Even though a reduction of aggregates should increase the Φ_F and Φ_Δ values, they must have decreased because of the environmental effect of a non-radiative process of electronic-to-vibrational energy transfer. The incorporation of PEG 400 increases the stability of liposomes.

P64

ELECTROGENERATED CHEMILUMINESCENCE FROM HYDROPHILIC AND HYDROPHOBIC CARBON NANOPARTICLES

Gabriela Marzari*, M. Sergio Moreno[+], Gustavo Morales* and Fernando Fungo*

[+] Centro Atómico Bariloche, San Carlos de Bariloche, Argentina. * Departamento de Química,
Universidad Nacional de Río Cuarto, Río Cuarto, Argentina.
E-mail:gmarzari@exa.unrc.edu.ar.

Palabras clave: Carbon Nanoparticles, Electrogenerated Chemiluminiscence, Nanomaterials.

Electrogenerated chemiluminescence (ECL) involves the generation of charged species at electrode surfaces undergo a highly exergonic reaction to produce an electronically excited state that then emits light. ECL biosensor, combines advantages from the selectivity of the biological recognition elements and the sensitivity of ECL technique; providing a powerful tool for ultrasensitive biomolecular detection and quantification. Nanomaterials have recently attracted the interest of many researchers in the field of biosensors owing to their unique physical and chemical properties, which have led to novel biosensors that exhibit high sensitivity and stability.[1] Most of the nanomaterials used in ECL are based on semiconductor and precious metal nanoparticles. However, they have in their composition toxic and expensive metals respectively. Recently, fluorescent carbon nanoparticles (CNPs) of low toxicity have been synthesized.[2] Herein, we present a simple and effective method for preparing ECL hydrophilic and hydrophobic CNPs which are suitable for further surface modification. The CNPs were synthesized by thermal treatment of molecular precursors. The graphitic nature and morphology of the resulting CNPs were analyzed by transmission electron microscopy (inset **Figure 1**). The electronic properties of CNPs were characterized by UV-vis absorption, photoluminescence (PL), electrochemistry and ECL. The fluorescent emission peaks of CNPs are shifted to longer wavelengths with increasing excitation energy. **Figure 1** show the ECL phenomenon obtained from CNPs in the presence of a coreactant (tri-*n*-butylamine). This preliminary work envisions promising applications into the area of biological labeling and biosensors.

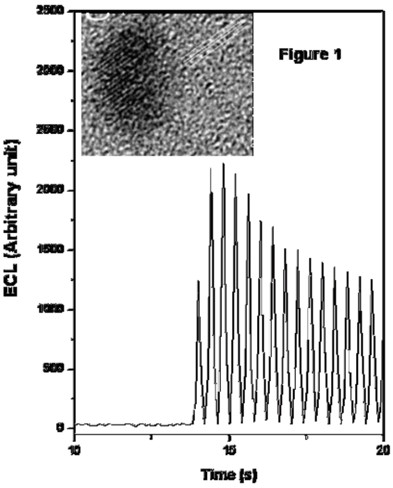


Figure 1

---

1 Honglan Qi, Yage Peng, Qiang Gao and Chengxiao Zhang. *Sensors* 9, **2009**, 674.

2 a) H. Zhu, X. Wang, Y. Li, Z. Wang, F. Yanga and X. Yang, *Chem. Commun.*, **2009**, 5118. b)F-R Fan, S. Park, Y. Zhu, R. S. Ruoff, and A. J. Bard *J. Am. Chem. Soc.* **2009**, *131*, 937.

P65

Propiedades Fotoquímicas, Fotofísicas y Láser de Hemicianinas

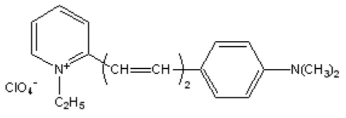
Walter Massad[1], Hernán Montejano[1], Norman García[1] , Daniel Mártire[2], Mónica González[2], Paula Caregnato[2], Laura Villata[2], Ángel Costela[3], Inmaculada García-Moreno[3]

[1] Departamento de Química, UNRC, Río Cuarto, Argentina
[2]INIFTA, UNLP, La Plata, Argentina
[3] Instituto de Química-Física “Rocasolano”, CSIC, Madrid, España.

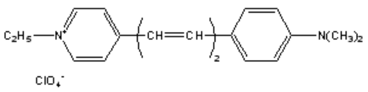
e-mail: hmontejano@exa.unrc.edu.ar

Palabras clave: hemicianinas; láser; colorantes

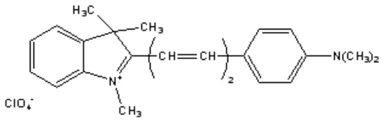
Las hemicianinas son moléculas iónicas con un grupo N,N-dimetilaminofenilo y un grupo N-alquilpiridinio en los extremos de una cadena carbonada insaturada, y resultan potencialmente aptas para ser empleadas como sondas fluorescentes, materiales activos para láseres de colorantes, biosensores y sensibilizadores. Sin embargo, escasos estudios han abordado la fotofisica y fotoquímica de los mismos. Estos colorantes absorben en la región azul-verde y emiten en la región roja del espectro.



LDS698



LDS722



LDS730

En este trabajo se ha realizado un análisis sistemático de las propiedades fotofísicas, fotoquímicas y de emisión láser de estos colorantes comerciales en función de la polaridad, viscosidad y temperatura del medio, con el fin de esclarecer la relación que existe entre estructura, propiedades y aplicaciones de los fluoróforos.

Estos colorantes presentan muy bajos rendimientos cuánticos de fluorescencia (Φ_f), son fuertemente dependientes de las propiedades del medio y poseen elevados desplazamientos de Stokes. Esto último sugiere que la excitación electrónica conlleva a un estado de transferencia de carga intramolecular (ICT), desde el grupo anilina hasta el grupo piridinio o 3-H-indolinio.

Por otra parte, los rendimientos cuánticos de triplete son extremadamente bajos, al punto que estos estados transitorios solo pudieron detectarse y cuantificarse en presencia de un exceso de IK. En estas condiciones se determinaron también los rendimientos cuánticos de fluorescencia y de formación de oxígeno molecular singlete.

Estos colorantes presentan una emisión láser estable entre 675-725 nm, con una eficiencia comprendida en el rango de 27-46%; la cual es favorecida en medios próticos de alta polaridad. Las características de la emisión láser se mantienen cuando estos colorantes se incorporan a matrices sólidas basadas en copolímeros de HEMA con monómeros sililados como TMSPMA. Todo indica que estos sistemas son susceptibles de ser usados como medios activos en láseres de colorante en estado sólido.

P66

THEORETICAL SPECTROSCOPY OF BILIN DYES IN PHYTOCHROMES

Ricardo A. Matute[†], **Renato Contreras**[†], **and Leticia González**[‡]

[†] Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653,
Santiago, Chile, matute@ciq.uchile.cl
[‡] Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena,
Helmholtzweg 4, 07743 Jena, Germany, leticia.gonzalez@uni-jena.de

Keywords: Phytochrome, Phytochromobilin, TDDFT

Phytochromes are important photoreceptors in plants, which regulates photomorphogenic responses (growth, flowering, shade avoidance, etc.) triggered by specific-wavelength light. Moreover, the phytochrome is considered a biological switch that photoconverts between a physiological inactive form called Pr (red-absorbing, ca. 666 nm) and a physiological active form called Pfr (far red-absorbing, ca. 730 nm) [1]. The mechanism involved in such photoconversion is not well understood, and one of the reasons is the limited number of crystallographic structures in the system. Therefore, we analyse the structure adopted by the different bilin dyes for phytochromes in proteobacteria, cyanobacteria, and plants; by means of subsystem-based theoretical spectroscopy [2], using the time-dependent density functional theory (TDDFT) for the calculation of excitation energies, and an implicit embedding method to describe the environment: unrelaxed x-ray structures of the chromophore together with a proper polarizable continuum model (PCM) representing the average electrostatic interaction with the environment. Thus, our theoretical approach predicted successfully the semicyclic structure ZZZssa for the phyocyanobilin chromophore in the cyanobacterial phytochrome Cph1 [3], and recently we have also predicted a semicyclic structure ZZZssa for the phytochromobilin chromophore in the plant phytochrome A [4].

Acknowledgements: Ricardo A. Matute thanks the Doctoral Fellowships from CONICYT and BECAS CHILE; and Leticia González thanks the financial support from the Deutsche Forschungsgemeinschaft (GO 1059/2-1).

References

[1]. N.C. Rockwell, Y.S. Su, and J.C. Lagarias, *Annu. Rev. Plant Biol.* **2006**, 57, 837.
[2]. J. Neugebauer, *ChemPhysChem* **2009**, 10, 3148.
[3]. R.A. Matute, R. Contreras, G. Pérez-Hernández, and L. González, *J. Phys. Chem. B* **2008**, 112, 16253.
[4]. R.A. Matute, R. Contreras, and L. González, *J. Phys. Chem. Lett.* **2010** (Submitted).

P67

ESTUDOS FOTOQUÍMICOS E FOTOFÍSICOS DO COMPLEXO *cis*-$[Ru(phen)_2(ImH)_2](PF_6)_2$

Regina Maria Mendes Oliveira[*], Carolina Riverin Cardoso[*], Míriam Nanami Numajiri [*], Rose Maria Carlos[*]

[*] Departamento de Química, Universidade Federal de São Carlos, São Carlos, Brasil, regynamendes@yahoo.com.br

Palavras Chaves: Complexo de rutênio, fotoquímica e fotofísica

Estudos da estrutura e reatividade de complexos de rutênio com ligantes polipiridínicos são de grande interesse, devido a sua versatilidade de aplicações como, por exemplo, sensores biológicos na determinação da concentração de oxigênio e CO_2, pH e temperatura e na análise dos sítios de ligação do DNA. A rigidez do anel polipiridínico permite que muitos destes compostos sejam emissivos quando irradiados com luz visível. Outro interesse do nosso trabalho é desenvolver um sistema de entrega de fármacos a partir da terapia fotodinâmica com a liberação de um princípio ativo que atue no tratamento de uma série de doenças do SNC. Com este interesse o ligante imidazol tem apresentado resultados promissores como um bom candidato a fármaco. Neste contexto o complexo *cis*-$[Ru(phen)_2(ImH)_2]^{2+}$ (RuImH) foi sintetizado, caracterizado e estudos fotoquímicos e fotofísicos foram realizados.

A fotoquímica foi acompanhada pelas técnicas de UV-vis, voltametria cíclica, RMN ^1H e emissão no solvente acetonitrila, usando um reator de 420 nm. O UV-vis do complexo RuImH possui um o λ_{max} de 481 nm e quando irradiado (por 20 minutos) o λ_{max} foi deslocado para 420 nm, cujo o comprimento de onda é característico do complexo *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$, de acordo com as equações 1 e 2.

$$cis\text{-}[Ru(phen)_2(ImH)_2]^{2+} \xrightarrow{CH_3CN} cis\text{-}[Ru(phen)_2(ImH)(CH_3CN)]^{2+} + ImH \quad (1)$$

$$cis\text{-}[Ru(phen)_2(ImH)(CH_3CN)]^{2+} \xrightarrow{CH_3CN} cis\text{-}[Ru(phen)_2(CH_3CN)_2]^{2+} \quad (2)$$

A fotólise acompanhada por RMN ^1H mostrou um sinal em 9,8 ppm característico do próton mais ácido da fenantrolina do complexo $[Ru(phen)_2(CD_3CN)_2]^{2+}$ e também o aumento da intensidade do sinal N-H do imidazol indicando a liberação deste ligante. O par redox do RuImH em 1,0/1,07 foi deslocado para 1,17/1,24 após a fotólise na voltametria cíclica, evidenciando a liberação do imidazol com a entrada do solvente acetonitrila, conforme a equação 1. A emissão em 660 nm foi suprimida durante a fotólise, sugerindo que o complexo *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ foi formado, uma vez que o mesmo não apresenta emissão.

Estes resultados são promissores, visto que os objetivos deste trabalho são a liberação do ligante imidazol via fotoquímica e a possibilidade da utilização de tal complexo como sonda molecular devido a sua luminescência.

P68

LIMITACIÓN DE LA ACCIÓN ANTIOXIDANTE DE FLAVONOLES DEBIDO A DEGRADABILIDAD POR ESPECIES RECTIVAS DE OXÍGENO FOTOGENERADAS

M. Paulina Montaña[1], Walter Massad[2], Susana Criado[2],
Alicia Biasutti[2] y Norman A. García[2]

[1] Instituto de Química de San Luis, Conicet - Univ. Nac. de San Luis. 5700 San Luis.
Argentina, mpaulina@unsl.edu.ar
[2] Dto. de Química. Univ. Nac. de Río Cuarto. 5800 Río Cuarto. Argentina.

Palabras clave: flavonol, fotooxidación, vitamina B2

La estructura de un flavonol (FL) consiste en un núcleo benzopiránico-4-ona con un grupo OH en C_3 y uno fenílico en C_4, como en los casos de: Quercetina (Que) (3,5,7,3´,4´,-pentahidroxiflavona) y Morina (Mor) 3,5,7,2´,4´-pentahidroxiflavona). Están presentes una inmensa variedad de productos vegetales[1], y generalmente se los presenta como agentes fotoprotectores frente a procesos oxidativos[2]. Reiteradamente se ha vinculado esta acción de los FLs con el número de grupos OH presentes y con la posición relativa de los mismos en la estructura molecular, pero sin llegar a establecerse patrones de comportamiento claros o definitivos[3]. A pesar de los muy numerosos estudios relacionados con la protección antioxidativa de los FLs, en general no se tiene en cuenta que en esa función son agentes "de sacrificio", ya que ellos mismos sufren degradación oxidativa.

En este trabajo hemos abordado un estudio sobre aspectos cinéticos y mecanísticos de la acción inhibidora de especies reactivas de oxígeno (EROs) fotogeneradas por la vitamina B2, también presente en numerosas especies vegetales y animales. Los FLs estudiados fueron Que y Mor, y el glicósido Rutina (Rut) (Que-3-D-rutinósido), con fines comparativos. Destacamos especialmente que el énfasis fue puesto en la fotodegradabilidad de los propios FLs.

La fotoirradiación con luz visible del soluciones acuosas formadas por vitamina B2 + FL genera distintas EROs, dependiendo del caso, que actúan sobre los propios FLs. Detectamos degradación de Que por las especies $O_2(^1\Delta_g)$, $O_2^{\bullet -}$ y H_2O_2, de Mor por $O_2(^1\Delta_g)$ y $O_2^{\bullet -}$ y de Rut, únicamente por $O_2(^1\Delta_g)$. Esto no significa que Mor y Rut no sean desactivantes de H_2O_2, sino que esta especie no se genera por fotoirradiación de las soluciones mencionadas. En términos generales la eliminación de un grupo OH en posición C_3 aumenta grandemente la estabilidad de Rut.

Medidas experimentales de consumo de oxígeno sobre las mezclas fotoirradiadas dan una escala de estabilidad de los FL como fotoprotectores antioxidantes en un medio simil-natural como el constituido por luz visible + Vitamina B2 + FL.

---

[1] E.Koh, KMS Wimalasari, AW Chassy, AE Mitchell, *J. Food Composition and Analysis* 22: 637-643, 2009.
[2] MP Montaña, NB Pappano, SO Giordano, P Molina, NB Debattista, NA García, *Pharmazie* 62 (1): 72-76, 2007.
[3] B Halliwell, *Archives of Biochemistry and Biophysics* 476: 107-112, 2008.

P69

SPECTRAL TUNING IN PHOTOACTIVE YELLOW PROTEIN BY MODULATION OF THE SHAPE OF THE EXCITED STATE ENERGY SURFACE

René Nome, [*] **Andrew Philip**[≠]**, George Papadontakis**[#]**, Norbert Scherer**[≠]**, and Wouter Hoff** [#]

* Instituto de Química, Unicamp, SP, Brasil
≠ Department of Chemistry, The University of Chicago, USA
\# Department of Microbiology and Molecular Genetics, Oklahoma State University, Stillwater, OK 74078, wouter.hoff@okstate.edu

Key words: wavelength regulation, photoreceptor, protein-chromophore interactions

Protein-chromophore interactions in photoreceptors often shift the chromophore absorbance maximum to a biologically relevant spectral region. A fundamental question regarding such spectral tuning effects is how the electronic ground state S0 and excited state S1 are modified by the protein. It is widely assumed that changes in energy gap between S0 and S1 are the main factor in biological spectral tuning. We report a generally applicable approach to determine if a specific residue modulates the energy gap, or if it alters the equilibrium nuclear geometry or width of the energy surfaces. This approach uses the effects that changes in these three parameters have on the absorbance and fluorescence emission spectra of mutants. We apply this strategy to a set of mutants of photoactive yellow protein (PYP) containing all 20 side chains at active site residue 46. While the mutants exhibit significant variation in both the position and width of their absorbance spectra, the fluorescence emission spectra are largely unchanged. This provides strong evidence against a major role for changes in energy gap in the spectral tuning of these mutants, and reveals a change in the width of the S1 energy surface. We determined the excited state lifetime of selected mutants, and the observed correlation between the fluorescence quantum yield and lifetime shows that the fluorescence spectra are representative of the energy surfaces of the mutants. These results provide strong evidence that residue 46 tunes the absorbance spectrum of PYP largely by modulating the width of the S1 energy surface.

P70

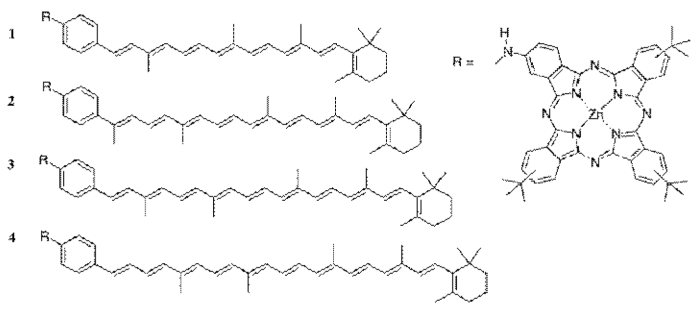
CAROTENOID PHOTOPROTECTION IN ARTIFICIAL PHOTOSYNTHETIC ANTENNAS

Smitha Pillai,[1] Miroslav K. Kloz,[2] Gerdenis Kodis,[1] John T. M. Kennis,[2] Rienk van Grondelle,[2] Devens Gust,[1] and Ana L. Moore[1]

[1]Department of Chemistry & Biochemistry and Center for Bioenergy and Photosynthesis, Arizona State University, Tempe, AZ, 85287-1605 and [2]Department of Biophysics, Division of Physics and Astronomy, Vrije Universiteit, 1081, Amsterdam

Key words: photosynthesis, photoprotection, carotenoids, fluorescence quenching

Non-photochemical quenching is a biological control system used by plants to match the rates of photogenerated chemical potential to the rates of non-photochemical, efficiency limiting, metabolic processes. The control system and the yield-limiting biochemistry must be optimized for photosynthesis to better meet societal energy needs. A new series of dyads (CPc) have been prepared featuring a secondary amine group as a bridge between the carotenoid (C) and a phthlocyanine (Pc); the carotenoid moieties contain 8 to 11 conjugated double bonds in addition to a phenyl group. Preliminary photophysical studies show that the S_1 state of Pc is considerably quenched by the attached carotenoid in polar and non-polar solvents. In toluene the degree of quenching depends on the length of the conjugated polyene; Pc fluorescence lifetimes with the major components (62 to 82 %) being 650 ps, 290 ps, 80 ps and 50 ps for the **1**, **2**, **3** and **4**, respectively (Pc model, 3 ns). The dyads in toluene have also been studied by pump-probe spectroscopy with both carotenoid (488 nm) and Pc (670 nm) excitation. In the EADS (evolution associated difference spectra) analysis, all components display bleaching both in the carotenoid and Pc region, but no carotenoid or Pc radical ions were detected implying that the quenching of ^{1}Pc is by an energy transfer mechanism from ^{1}Pc to the carotenoid S_1 state. Generally, the time constants of the second component (which should be the Pc singlet lifetime) agree with the fluorescence lifetime data and correlate with the length of the polyene chain. No obvious component associated with inverted kinetics was observed in the transient absorption data, which contrasts with the situation of the dyads in which the carotenoid with a conjugated carbonyl group formed an amide with Pc. Rather, a carotenoid S_1-like signature was present in the transient spectra immediately after Pc excitation. This observation suggests that in the present dyads, the quenching cannot be described with a simple sequential ^{1}Pc → carotenoid S_1 energy transfer scheme. Possibly, the quenching is mediated through excitonic coupling between the ^{1}Pc and the optically forbidden S_1 and/or S* state, as previously proposed to occur in LHCII. The fluorescence lifetime in polar solvents indicate stronger quenching of ^{1}Pc by the attached carotenoid (e.g., 40 ps for **3** in benzonitrile) and in THF transient absorption experiments on **3** clearly showed absorption at 980 nm, which is characteristic of both $C^{\bullet+}$ and $Pc^{\bullet-}$.



P71

ACTIVACIÓN DEL PEROXODISULFATO POR MEDIO DE CU(II) Y LUZ SOLAR. SU APLICACIÓN A AGUAS CONTAMINADAS CON NAFTA.

Verónica Mora[1], Mónica Gonzalez[1], Daniel Mártire[1], Lucas Santos Juanes[2], Antonio Arques[2]

(1) INIFTA, Departamento de Química, Facultad de Ciencias Exactas, UNLP, CC 16, Sucursal 4, (1900) La Plata, Argentina. e-mail: gonzalez@inifta.unlp.edu.ar

(2) Departamento de Ingeniería Textil y Papelera. Escuela Politécnica Superior de Alcoy, Universidad Politécnica de Valencia. Plaza Ferrándiz y Carbonell s/n, 03801 Alcoy

Palabras claves: ISCO, peroxodisulfato, nafta

Debido a la gran cantidad de derrames de gasolina y petróleo que ocurren durante su transporte y almacenamiento, resulta de interés el estudio de la remediación por métodos ISCO (in situ chemical oxidation) de estos contaminantes en tierras y en aguas subterráneas. En los últimos años se comenzó a utilizar el peroxodisulfato ($S_2O_8^{2-}$), oxidante de fácil manejo y transporte en aplicaciones ambientales reales. El radical sulfato ($SO_4^{\bullet -}$), intermediario reactivo responsable de la eficiencia oxidativa de estos procesos presenta una gran capacidad oxidante. Los metales de transición pueden actuar como fotocatalizadores para activar el $S_2O_8^{2-}$,cuando se irradia la mezcla con luz UV-vis. Por tanto, se puede utilizar luz solar como fuente de radiación con las importantes ventajas económicas y ecológicas que conlleva.

En el presente trabajo se emplea Cu(II) y luz solar para activar al $S_2O_8^{2-}$ en la detoxificación de un efluente contaminado con naftas, con el fin que los procesos biológicos más baratos y eficientes, se encarguen de eliminar la materia orgánica biodegradable.

La fotólisis de soluciones con 20 ppm de Cu(II) y concentraciones iniciales variables de $S_2O_8^{2-}$ muestran que la velocidad de mineralización no depende, dentro del error experimental, de la concentración de $S_2O_8^{2-}$, salvo cuando este se convierte en el reactivo limitante. De hecho, el agregado periódico de pequeñas cantidades de $S_2O_8^{2-}$ a estas soluciones mejora la disminución del TOC (carbono orgánico total). Por otro lado, la fotólisis de soluciones con concentraciones iniciales fijas de $S_2O_8^{2-}$ y diferentes concentraciones de Cu(II) en el intervalo de 20 a 1000 ppm muestran similares velocidades de mineralización.

En los ensayos realizados con agua contaminada con nafta, 20 ppm de Cu(II) y agregados de peroxodisulfato 2.6 x 10^{-5}M cada 60 minutos durante 3 horas, el índice de biodegradabilidad dado por la relación DBO_5 (demanda bioquímica de oxígeno)/DQO (demanda química de oxígeno) se inicia en el valor de 0.01 y al termino de la reacción el valor no supera 0.14. Estos resultados indican que el tratamiento mejora lentamente la calidad de las aguas a pesar de que durante un período de 3 hs no disminuye el contenido de TOC ni se alcanza un valor aceptable del indicador de biodegradabilidad ya que para ello la relación DBO_5/DQO debe superar el valor 0.2. Este comportamiento es esperable debido al alto contenido inicial de hidrocarburos en las muestras.

P72

REACTIVIDAD DE MORINA CON OXÍGENO MOLECULAR SINGULETE EN MEDIO HOMOGENEO, SOLUCIÓN DE LIPOSOMAS Y MEMBRANAS DE ERITROCITOS

Javier Morales[1], Francesca Casanueva[1], Patricio Bustos[1],
Germán Günther[2], Antonio L. Zanocco[2] y Else Lemp[2]

[1] Depto. de Ciencias y Tecnología Farmacéuticas. [2] Depto. de Química Orgánica y Fisicoquímica. Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile.
Sergio Livingstone 1007 Independencia, Santiago, Chile,
javierm@ciq.uchile.cl, elemp@ciq.uchile.cl

Palabras clave: morina, flavonoides, oxígeno molecular singulete

Los flavonoides son compuestos polifenólicos ampliamente distribuidos en el reino vegetal. Dentro de sus múltiples beneficios para la salud, destacan sus propiedades antioxidantes contra el daño que producen los radicales libres y otras especies reactivas como el oxígeno molecular singulete.

En este trabajo se estudió la reactividad morina con oxígeno molecular singulete en distintos medios. No existen antecedentes en literatura sobre la reactividad de este flavonoide con oxígeno excitado. Estructuralmente, morina es similar a quercetina (flavonoide más representativo) siendo su única diferencia en la posición del grupo hidroxilo R2´y R3´ en el mismo anillo, respectivamente.

Se determinaron constantes experimentales de reacción (k_{EXP}) y constantes de velocidad de reacción química (k_R) para la reacción entre el O_2 ($^1\Delta_g$) y morina, en medio homogéneo (etanol, metanol, mezclas acuosas y otros alcoholes) y en sistemas microheterogeneos (liposomas de dipalmitoilfosfadidilcolina y membranas de eritrocitos). Las metodologías analíticas utilizadas fueron la espectrofotometría ultravioleta visible y la cromatografía líquida de alta eficiencia. Además, se hicieron mediciones con pruebas fluorescentes (DPH y laurdan) para estimar la ubicación relativa de morina en la membrana fosfolipídica.

Medio	k_{EXP}^{morina} (s^{-1})	$k_{EXP}^{quercetina}$ (s^{-1})	$k_R^{morina}/k_R^{quercetina}$
Isopropanol	$9,29 \times 10^{-4}$	$2,08 \times 10^{-4}$	4,47
Tampón pH 7,4	$3,36 \times 10^{-3}$	$7,27 \times 10^{-4}$	4,62
Liposomas 5,0 mM	$3,19 \times 10^{-3}$	$1,18 \times 10^{-4}$	27,03
Liposomas 10 mM	$3,68 \times 10^{-3}$	1.26×10^{-4}	29,20
Membranas eritrocitos A	$1,08 \times 10^{-3}$	$1,94 \times 10^{-4}$	5,57
Membranas eritrocitos B	$2,79 \times 10^{-3}$	$5,09 \times 10^{-4}$	5,48

La reactividad frente al oxígeno molecular singulete, de morina es mayor a la reactividad de la quercetina, cuando el medio es homogéneo. Un comportamiento equivalente se observa cuando los flavonoides son incorporados a membranas de eritrocitos, inclusive con un orden similar entre las constantes. Sin embargo, la reactividad de quercitina en liposomas de DPPC se observa muy disminuida en relación a morina, posiblemente debido a la diferente ubicación de ambos flavonoides en la bicapa lipídica.

P73

Chiral probe interaction with lanthanide achiral complexes

Alvaro Muñoz-Castro[*], **Ricardo Veloso*, Desmond Mac-Leod Carey*, Ramiro Arratia-Perez***

* Departamento de Ciencias Químicas, Universidad Andrés Bello, Republica 275, Santiago, Chile, armunozc@gmail.com

Palabras clave: Chiral Probe, Lanthanide, Double-Groups, Pfeiffer effect

The interaction between an achiral chromophore and chiral nonchromophore, has proven to be an useful and reliable method for probing the chirality of the nonchromophore molecule using circular dichroism (CD) techniques[1]. The use of the achiral chromophore complex of lanthanide (III) (Ln= Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm) tris 2,2'-oxydiacetic acid (oda) (Figure 1), which exist in a racemic equilibrium, with *L*-proline and *D*-proline gave a CD active signal that include a Ln ↔ Ln transition[1], due to the shift in the racemic equilibrium (Pfeiffer effect[2]). In order to gain more insight into the CD activation of the Ln ↔ Ln transition of the $[Ln(oda)_3]^{3-}$ series, relativistic DFT calculations were carried out including both scalar and spin-orbit effects. The transitions were treated according to the *j-j* coupling scheme using the D_3* double valued point group instead of the spherical symmetry, which is typical used within Ln-Ac complexes.

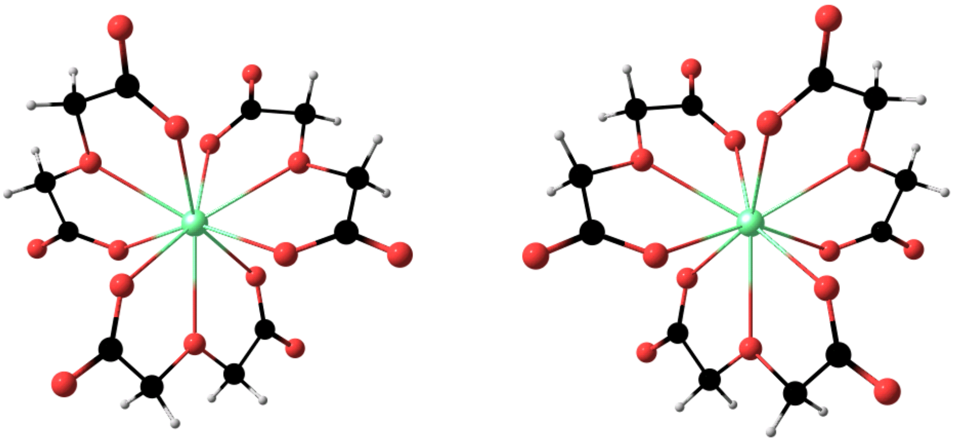


Figure 1. Scheme of the two isomers of $[Ln(oda)_3]^{3-}$, which belong to the D_3 point group.

BIBLIOGRAPHY

[1] Parac-Vogt, T. N., Binnemans, K., Göller-Walrand, C., ChemPhysChem **2001**, 767.

[2] Pfeiffer, P, Quehl, K., Chem. Ber. **1931**, 64, 2667.

ACKNOWLEDGMENT: This work has been supported by projects FONDECYT Grants 1070345, UNAB-DI-02-09/R, UNAB-DI-09-09/I, UNAB-DI-06-09/I, PROJECT MILLENNIUM No. P07-006–F, Beca Doctoral UNAB.

P74

PHOTOCHEMISTRY OF AFLATOXINS B_1 AND B_2

José Carlos Netto-Ferreira[1,2], **Belinda Heyne,**[2] **Juan C. Scaiano**[2]

[1] Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Brazil.
[2] Division of Chemistry, University of Ottawa, Canada.
jcnetto@ufrrj.br

Keywords: Aflatoxins; laser flash photolysis; Photoionization; singlet oxygen.

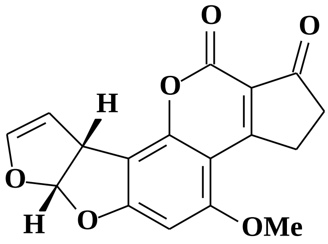
Aflatoxins B_1 and B_2 are the most toxic among the known aflatoxins produced by several strains of the genus *Aspergillus (Aspergillus flavus*, *Aspergillus parasiticus* and *Aspergillus nomius)*, being widely spread in the tropics and subtropics. They are known to be hepatotoxic, hepatocarcinogenic, teratogenic and mutagenic.

Laser excitation (308 nm) of a nitrogen purged solution of Aflatoxin B_1, in acetonitrile, results in the formation of a transient (λ_{max}=480 nm, bleaching at 320 and 350 nm; τ=7.4 μs) that was quenched by oxygen and β-carotene at a diffusion-controlled rate constant. This transient was assigned to the triplet state of Aflatoxin B_1. Similar results were obtained for Aflatoxin B_2, in acetonitrile.

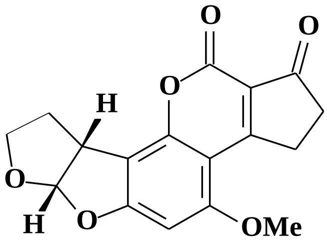
Photolysis (308 nm) of a nitrogen degassed solution of either Aflatoxin B_1 or B_2 in phosphate buffer solution (PBS) (pH=7.4) leads to the formation of a strong and broad signal in the 600-750 nm region (λ_{max}=640 nm). This transient was quenched by oxygen and was assigned to the solvated electron. The quantum yields of solvated electron formation, which also correspond to the photoionization quantum yield for the aflatoxins B_1 or B_2, were 0.11 and 0.29, respectively.

Laser excitation (λ=248 nm) of Aflatoxin B1 or Aflatoxin B2 in oxygen saturated 0.1 $molL^{-1}$ sodium dodecyl sulfate (SDS) solution leads to the formation of a transient showing maxima at 600 and 650 nm, together with a shoulder at 680 nm. This transient was assigned to the corresponding cation radicals derived from aflatoxins B_1 or B_2.

Singlet oxygen was readily formed through a triplet-triplet energy transfer process, employing either Aflatoxin B_1 or B_2 as the photosensitizer, and quantum yields of singlet oxygen formation ($\Phi_\Delta\ {}^1O_2$) of 0.51 and 0.59, respectively, were measured.



Aflatoxin B_1



Aflatoxin B_2

P75

DEGRADATION OF IRON(III)- SALICYLATE COMPLEXES IN FENTON SYSTEMS. EFFICIENCY OF IRON(II) PHOTOPRODUCTION.

Daniela Nichela[*], **Menana Haddou**[#], **Andrés Donadelli***, **Esther Oliveros**[#], **Fernando García Einschlag***

[*] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Dep. de Química, Fac. de Cs Exactas, UNLP, CONICET, La Plata, Argentina. **e-mail: dnichela@inifta.unlp.edu.ar**
[#] Laboratoire des IMRCP, Université Paul Sabatier (UPS, Toulouse III), 118 rte Narbonne, France

Keywords: Fenton, benzoic acid derivatives, polychromatic quantum efficiency

Photo-reduction by inner-sphere electron transfer (LMCT) of Fe(III)-aquo complexes provide an important route for Fe(III) reduction in photo-Fenton systems that substantially increase the rates of Fe(II) and HO· production:

$$[Fe(III)(OH)^-]^{+2} + h\nu \rightarrow Fe(II) + HO\cdot \qquad (R1)$$

In the present work, photo-Fenton techniques have been used for the degradation of a set of hydroxyl-derivatives of benzoic acid. The studied model substrates (L) were the following ones: 2-hydroxybenzoic acid (2H-BA); 2,4-dihydroxybenzoic acid (24DH-BA); 2-hydroxy 5-nitrobenzoic (2H5N-BA) and 2-hydroxy 4-nitrobenzoic acid (2H4N-BA). Previous work has shown that, in Fe(III)-containing solutions, the studied substrates form highly stable complexes with stoichiometries 1:1 or 2:1

$$LH^- + Fe(III) \rightarrow [Fe(III)L]^+ + H^+ \qquad (R2a)$$

$$2\,LH^- + Fe(III) \rightarrow [Fe(III)L_2]^- + 2\,H^+ \qquad (R2b)$$

In this study, we have focused on the efficiency of Fe(II) and HO· photo-production by the latter iron(III)-complexes. Concentration profiles of Fe(II) were studied in the absence of H_2O_2, since ferrous species react very quickly with hydrogen peroxide. Two sets of experiments were performed. In the first set we irradiated Fe(III) solutions of each substrate and recorded the Fe(II) profiles. During the first minutes, the amounts of produced Fe(II) decrease in the following order:

Fe(III).Aq > 24DH-BA > 2H-BA > 2H4N-BA > 2H5N-BA

HPLC analyses showed an important degradation of the irradiated substrates. Since reaction intermediates may affect Fe(II) production, we performed a second set of experiments in the presence of 0.019 M of benzene as HO· scavenger. Both Fe(II) and HO· productions were analyzed and the following trend was observed:

Fe(III).Aq > 2H-BA > 24DH-BA > 2H4N-BA > 2H5N-BA

This confirms that reaction intermediates strongly affected Fe(II) production in the first set of experiments. Thus, Fe(II) profiles obtained in the presence of benzene were used to evaluate the polychromatic quantum efficiencies. The results show that irradiation of Fe(III)-complexes is less efficient than the photo-reduction of Fe(III) aquo complexes.

P76

A FLUOROGENIC CHEMOSENSOR FOR CN^- BASED ON A DISPLACEMENT ASSAY INVOLVING A 1,8–NAPHTHYRIDINE AND Cu(II)

Celso R. Nicoleti, Diogo N. Garcia, Iêda M. Begnini, Ricardo A. Rebelo, and
Vanderlei G. Machado[*]

[*] Departamento de Química, Universidade Regional de Blumenau, FURB, Blumenau, SC, 89012–900. e–mail: gageiro@furb.br

Keywords: fluorogenic chemosensors; anion sensing; cyanide

Indicator–displacement assays have been used in the last few years to develop chromogenic and fluorogenic chemosensors for a large diversity of analytes [1]. Two 1,8–naphthyridines, **1** and **2**, were synthesized (**Figure 1a**) and their spectroscopic properties were studied. These compounds revealed to be fluorescent, giving the following data in water (pH 7.0, tris–HCl): **1**, 2.0×10^{-6} mol L^{-1}, $\lambda_{max}^{exc} = 321$ nm, $\lambda_{max}^{em} = 470$ nm, $\phi = 0.0460$; **2**, 1.3×10^{-6} mol L^{-1}, $\lambda_{max}^{exc} = 326$ nm, $\lambda_{max}^{em} = 402$ nm, $\phi = 0.0753$. The addition of Cu(II) to the solutions of **1** and **2** in water and water–DMSO mixtures was responsible for the complete quenching in the fluorescence of the compounds. After, a study was made by adding increasing amounts of CN^- as a tetra–*n*–butyl ammonium salt (in DMSO) or as a sodium salt (in aqueous solutions). It was verified that the addition of this anion caused the reappearance of the emission band. This can be explained by the fact that CN^- makes strong complexes with Cu(II) cation. Thus, the presence of the anion in solution creates a competition scenario, of the naphthyridine and CN^- for the cation. The decomplexation of Cu(II) from the binding site in the compound leads to the restoration of its fluorescence.

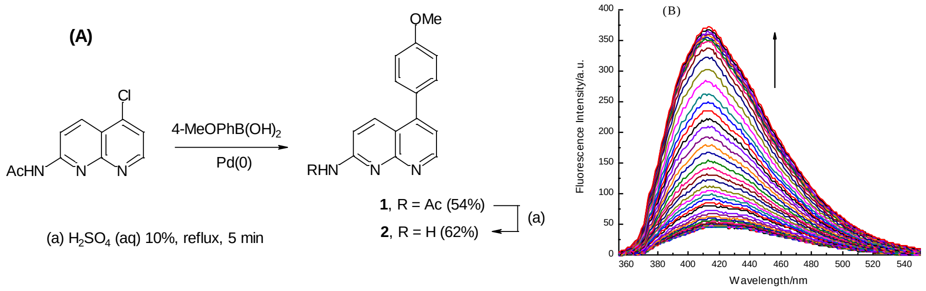


Figure 1. (A) Schematic representation for the syntheses of **1** and **2**. **(B)** Titration of (**2**:Cu^{2+}) with NaCN in DMSO–water (7:3 vol/vol; pH 8.5, tris–HCl).

Titration experiments demonstrated the need of two equivalents of CN^- in the mixture containing Cu(II) and the naphthyridine to increase the intensity of the fluorescence emission to its maximum level, which corresponded exactly to the same value before the addition of the metal ion to the naphthyridine solution. A study was made to verify the influence of other anions on this system, being observed that $H_2PO_4^-$ and F^- also caused a restoration of the fluorescence of the free naphthyridine, but to a lesser extent than CN^- (40% for $H_2PO_4^-$ and 30% for F^-). [FURB, CNPq, INCT–Catálise]

[1] Nguyen, B.T.; Anslyn, E.V. *Coord. Chem. Rev.* **2006**, *250*, 3118.

P77

PHOTOPYSICAL PROPERTIES OF SUNSET YELLOW DYE IN BIOPOLYMERS

<u>Ives Tulio Oliveira dos Santos</u>, Rayara Ribeiro de Souza and Jacques Antonio de Miranda

Instituto de Ciências Ambientais e Desenvolvimento Sustentável, Universidade Federal da Bahia, Barreiras, Brasil, R. Prof. José Seabra s.n., jacques.miranda@ufba.br

Key Words: Sunset Yellow, amylopectin, starch

Biopolymers as starch and derivatives have a broad application field in food, paper, and plastic industries [1,2], because of the low cost and widespread availability of the former. A very interesting application of starch is the biodegradability enhancement of resins or the plastic matrix when it is added as blend [3–5]. Their use can improve the properties of dyes and pigments by food industry.

In this work, some photophysical properties of Sunset Yellow (INS 110), in several alcohols, starch and potato amylopectin suspensions (0.1% w/v) are under investigation.

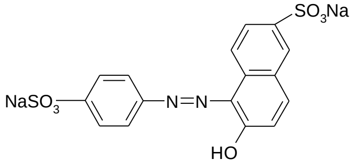


Fig.1. Sunset Yellow

The absorption spectra of this dye shows maxima at 478 – 488 nm in all systems studied. These values showed dependent of polarizabity index of solvent. The dye exhibit a hypsochromic shift when the polarity of the alcohol also increases.

The maximum absorption observed for the dye in water was 483 nm, which suggests a very specific interaction between the species. When the data are analyzed according to the polarization orientation, note that the photophysical properties of the dye in water follows a distinct pattern to that observed in alcohols, suggesting that they were important interactions with nonpolar parts of the structure of alcohols.

In the suspensions of biopolymers, the maximum absorption observed were similar to those obtained in ethanol, suggesting that even if the dye is very soluble in water, it occupies a region with characteristics similar to that alcohol.

Another factor that draws attention in relation to the conduct of Sunset Yellow in biopolymers with respect to the increased intensity of the absorption band compared with the dye in water. This result suggests that thin films, suspensions or microspheres available, based on starch derivatives may be of interest to the food industry, since the same staining observed in water could be obtained with a smaller amount of dye in the presence of biopolymer.

[1] R. Chandra, R. Rustgi, Prog. Polym. Sci. 23 (1998) 1273.
[2] S. Jobling, Curr. Opin. Plant Biol. 7 (2004) 210.
[3] H.A.A. El-Rehim, E.-S.A. Hegazy, A.M. Ali, A.M. Rabie, J. Photochem.Photobiol. A 163 (2004) 547.
[4] R.P. Singh, J.K. Pandey, D. Rutot, P. Deg´ee, P. Dubois, Carbohydr. Res.338 (2003) 1759.
[5] X. Ramis, A. Cadenato, J.M. Salla, J.M. Morancho, A. Vall´es, L. Contat,A. Ribes, Polym. Degrad. Stab. 86 (2004) 483.

P78

CHARACTERIZATION OF SUCROSE ESTER REVERSED MICELLES

Anakenna Ortega, Karina Castillo, Paulina Fernández, Antonio Zanocco, German Günther

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

Keywords: Sucrose esters, reversed micelles.

In the present study we synthesized and purified several 6-O-sucrose monoesters and 6-O, 6-O’ sucrose diesters having different alkyl chain lengths by using synthetic methods under Mitsunobu conditions. For all the available compounds the physico-chemical information concerning the formed reversed micellar aggregates in chloroform was evaluated by using spectroscopic or fluorescent methodologies.

Cmc values for the series show a fair direct dependence with the temperature depending on the fluorescent methodology employed (polarization or intensity).

To probe the structure of water inside the micelles we analyzed the acid base equilibrium of pyranine. At high *R* values the behavior is like in homogeneous water solution, while at low *R* values the interaction water molecules with sucrose moieties avoids the probe acid-base dissociation, the emission from dissociated probe is only observed for R values higher than 10 for all the studied esters.

The results obtained show for 6-O sucrose mono esters with different length of alkyl chain that its micellar properties show a fair dependence on the balance of the size of alkyl chain and the sucrose head .

Financial support from Fondecyt 1080412 is gratefully acknowledged by G. G.

P79

“PROPIEDADES AMPLIFICADORAS DE NANOPARTÍCULAS DE PLATA APLICADAS A LA FLUORESCENCIA DE MACROCICLOS TIPO PORFIRINA”

Victoria Ortega V., Víctor Vargas C. y Hernán E. Ríos
Departamento de Química, Facultad de ciencias, Universidad de Chile, Santiago, Chile.
victoriapatricia@gmail.com

Palabras clave: porfirinas, fluorescencia amplificada, nanopartículas.

En este trabajo se presenta un estudio del aumento de la intensidad de la señal fluorescente de meso-Tetrafenilporfirina (TPP), Tetrapiridilporfirina (TPyP), Protoporfirina IX (PPIX) depositada sobre una superficie rugosa de plata en función de la longitud de onda de excitación y en función de la distancia fluoróforo-superficie[1].

La superficie con nanoestructura de plata es preparada sumergiendo por 48 hrs., un vidrio pyrex silanizado con 3-aminopropiltrietoxysilano (APS) en una solución coloidal de plata, la que es obtenida empleando hidroxilamina como agente reductor.

El estudio de la intensidad de fluorescencia en función de la distancia de separación fluoróforo superficie metálica, se realiza empleando dos técnicas: 1) Layer by Layer (LBL)[2], en que cada bicapa está formada por clorhidrato de polialilamina (PAH, polielectrolito catiónico) y poliestirensulfonato (PSS, polielectrolito aniónico) y 2) una capa de polielectrolito catiónico de poli-(dimetil amino etilmetacrilato), cuaternizado con bromuro de alquilo de 8, 10, 12 y 14 átomos de carbono. En el primer caso el máximo de la intensidad de la señal fluorescente se obtiene en la bicapa número 5 y en el segundo se obtiene importantes incremento en la señal fluorescente para los polímeros que poseen 8 y 10 átomos de carbono en su cadena alquílica.

En el estudio del incremento de la señal fluorescente en función de la longitud de onda de excitación, se realiza comparando la intensidad de la fluorescencia obtenida excitando los sistemas moleculares en la región de la banda de Soret (400-420 nm) y en la primera banda Q (500-514 nm). El resultado muestra que existe una mayor eficiencia en la amplificación de la señal cuando la excitación es en la banda Q.

AGRADECIMIENTOS: Beca doctoral CONICYT y Proyecto AT. Nº 24090169.

---

[1] “Metal-Enhanced Fluorescence”, Chris D. Geddes, J. R. Lakowicz, Journal of Fluorescence, vol. 12. Nº2, June 2002.

[2] M. Kolasinska, P. Warszynski, *Bioelectrochemistry*, 2005, **66**, 65-70.

P80

MECHANISM OF QTX DYE DEGRADATION IN AQUEOUS SOLUTION

Josy A. Osajima[1], José Carlos Netto Ferreira, Carla C. C. Schmitt[2], Miguel G. Neumann[2]

[1]Universidade Federal do Piauí, Bom Jesus, Piauí, Brasil
[2]Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil
josy_osajima@yahoo.com.br

Palabras clave: photoproducts, photodegradation, QTX, dye

The mechanism of QTX [2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethyl-1-propanium chloride] dye degradation in aqueous solution was investigated. The photoproducts generated upon its photolysis were characterized by HPLC/ESI/MS. The dye photooxidation was monitored by electronic absorption spectroscopy. Ground state absorption spectrum of the dye revealed bands at 273 nm and 402 nm. After 160 h irradiation, the absorption intensity at 402 nm and 273 nm decreases together with the appearance of a new band near 310-350 nm, typical of oxidized QTX. The chromatogram obtained after 160 h irradiation of QTX shows the appearance of new peaks due to photoproducts resulting from QTX degradation and they are identified by mass spectrometry. The mass spectrum shows peaks at m/z 388, 420 and 270 attributed to photoproducts with the peak at m/z 372 being due to QTX. The peak at m/z 388 is due to the formation of the sulfoxide derived from QTX, whereas the two photoproducts with peak at m/z 420 suggested the formation of the sulfone derived from QTX as well as to the sulfoxide containing hydroxyl groups in both methyl groups. The peak at m/z 270 suggests that the singlet oxygen react formed energy transfer from triplet QTX abstracts hydrogen from the carbon bonded to the hydroxyl, with the subsequent release of the amino group. Rearrangement of QTX molecule leads to the product having m/z 270.

The elementary reactions of QTX in aqueous solution were investigated by laser flash photolysis. The quenching rate constant for the triplet excited state of QTX in the presence of potassium sorbate and hydroquinone were close to the value of diffusion-controlled rate constant. It was possible to propose a mechanism for QTX degradation combining the results from the different techniques. When potassium sorbate was employed as the quencher an increase of QTX degradation percentage was observed. These results suggested that the mechanism of QTX degradation occurs mainly through a singlet excited state.

The authors thank FAPESP and CNPq for financial support.

P81

CHARACTERIZATION OF BACTERIA USING ITS O-ANTIGEN WITH SURFACE-ENHANCED RAMAN SCATTERING

<u>Igor Osorio-Román</u>[a], Ricardo Aroca[b], Jason Astudillo[a], Betty Matsuhiro[a], Claudio Vásquez[c] and José Pérez[c]

[a] Department of Environmental Chemistry, Faculty of Chemistry and Biology, Universidad de Santiago de Chile, Av. B. O'Higgins 3363, Santiago, Chile. email: igor.orlando@gmail.com
[b] Department of Chemistry and Biochemistry, Faculty of Sciences, University of Windsor, 273-1 Essex Hall, 401 Sunset Avenue, Windsor, Canada.
[c] Department of Biology, Faculty of Chemistry and Biology, , Universidad de Santiago de Chile, Av. B. O'Higgins 3363, Santiago, Chile.

Keywords: bacteria; antigen; surface-enhanced Raman scattering

The O-antigen determines the specificity of each bacterial serotype, a kind of fingerprint for bacteria[1]. In this report we explain the extraction, purification and characterization of two O-antigen of pathogenic bacteria (*Escherichia coli* O16 and *Salmonella* Typhimurium). The molecular fingerprints, found in the vibrational spectra, represent the most powerful analytical technique for identification (or differentiation) of molecular moieties in complex systems such as pathogens. In addition, the advantages of vibrational Raman are compounded with the high sensitivity achieved using Surface-enhanced Raman scattering (SERS). SERS is used here to take advantage of the vibrational differences in the O-antigens, allowing the differentiation between these two bacteria. Characteristic fundamental vibrational modes associated with the monosaccharide, N-acetylglucosamine and deformations in the O-antigen chains provide the main spectroscopic differences between the O-antigen of *E. coli* O16 and *S.* Typhimurium (see figure 1).

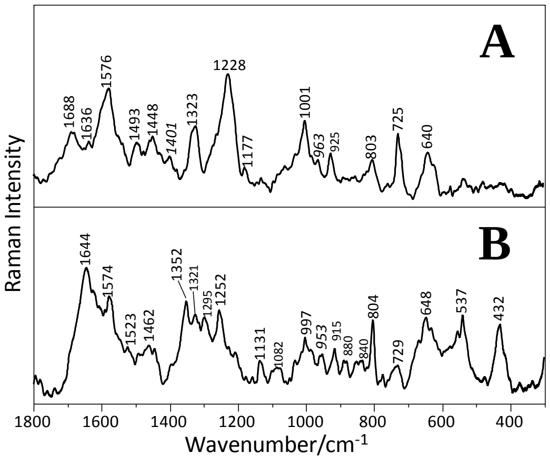


Figure 1. SERS spectra of O-antigen on silver colloid solution of *E. coli* O16 (A) and *S.* Typhimurium (B).

References

1.- I.O. Osorio-Román, R.F. Aroca, J. Astudillo, B. Matsuhiro, C. Vásquez and J. Pérez, *Analyst*, 2010, DOI: 10.1039/C0AN00061B.

P82

UNA POSIBLE VIA DE FOTOGENERACIÓN NATURAL DE ACIDOS HÚMICOS

Adriana Pajares[1], José Gianotti[1], Mabel Bregliani[1] , Isela Gutiérrez[2], M. Paulina Montaña[3], Walter Massad[4], Susana Criado[4], y Norman A. García[4]

[1] Unidad Académica Río Gallegos. Univ. Nac. de la Patagonia Austral. 9400 Río Gallegos. Argentina. apajares@speedy.com.ar
[2] Dto. de Química. FCN. Univ. Nac. de la Patagonia SJB. 9000 Comodoro Rivadavia. Argentina
[3] Area de Química-Física, Univ. Nac. de San Luis, 5700 San Luis. Argentina
[4] Dto. de Química. Univ. Nac. de Río Cuarto. 5800 Río Cuarto. Argentina. ngarcia@exa.unrc.edu.ar

Palabras clave: ácido gálico, ácido húmico, fotodegradación

Las características comunes del ácido gálico (GA) con los ácidos húmicos (HA) y fúlvicos (FA) de poseer estructuras aromáticas polihidroxiladas y formar quelatos con diversos metales[1],[2] constituyen una invitación al estudio de algunas reacciones del primero como modelo muy simplificado del comportamiento de estos importantes componentes orgánicos de los suelos (HA y FA).

Se investigó dentro de las posibles fotoreacciones precursoras en la generación de sustancias húmicas, la interacción promovida entre luz visible y (Rf), un fotosensibilizador natural en sistemas acuosos, y ácido gálico (GA) un polifenol naturalmente formado después de la degradación de la lignina. En esta contribución presentamos un estudio sistemático de la cinética y mecanismos bajo condiciones aeróbicas en medios acuosos, por medio de fotólisis continua de luz visible, detección polarográfica de consumo de oxígeno, espectroscopía fluorescente estacionaria y resuelta en el tiempo, detección de fosforescencia resuelta en el tiempo y técnicas de láser flah fotólisis. GA se degrada relativamente rápido en soluciones acuosas pH 7, donde el oxígeno singlete molecular ($O_2(^1\Delta_g)$), el anión radical superóxido ($O_2^{\bullet-}$) y el peróxido de hidrógeno (H_2O_2) – tres especies fotogeneradas desde el triplete excitado de la Rf–, participan en los fotoprocesos.

La conclusión general es que en aguas naturales el GA puede fotodegradarse espontáneamente en condiciones ambientales Las especies radicalarias generadas en presencia de Rf pueden participar de las reacciones de condensación o polimerización promoviendo la síntesis natural de productos húmicos, procesos que ya han sido propuestos y alcanzados recientemente por medio de reacciones térmicas[3].

---

[1] Environmental Pollution, 140, 2006, 114-123

[2] Colloids and Surfaces B: Biointerfaces, 13, 1999, 127-134

[3] Journal of Colloid and Interface Science, 336, 2009, 59–66.

P83

FOTOQUÍMCA DE UNA α-OXOAMIDA-ETER CORONA EN PRESENCIA DE IONES METALICOS EN ACETONITRILO

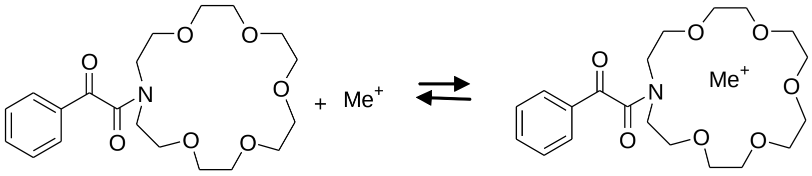
Cecilia M. Palacios, Sonia Bertolotti, Carlos Previtali y Carlos Chesta.

Departamento de Química, Facultad de Ciencias Exactas Físicoquímicas y Naturales, Universidad Nacional de Río Cuarto, 5800-Río Cuarto, Argentina. Email: cpalacios@exa.unrc.edu.ar

Palabras clave: α-oxoamida-éter-corona, complejación, transitorios.

Las α-oxoamidas son compuestos no fluorescentes que tras irradiación con luz UV producen fotoproductos de interés farmacológico. Se ha propuesto que los fotoproductos derivan de dos tipos de intermediarios de reacción, uno dirradicalario (D) y otro zwitteriónico (Z). La ciclización del dirradical produce una β-lactama, mientras que el ataque nucleofílico del oxígeno a la unión imida del zwitterión lleva a la obtención de la oxazolidinonas. La distribución de fotoproductos depende de la naturaleza de los sustituyentes y de la polaridad del medio, dado que estos afectan la cinética de formación y estabilidad relativa de los intermediarios de reacción.

Presentamos aquí un estudio sobre la fotofísica / fotoquímica de una oxoamida-éter corona (**I**) en la ausencia/presencia de iones metálicos alcalinos y alcalineos térreos. El objeto de este estudio es investigar si los metales acomplejados son capaces de modificar la reactividad de la amida alterando la estabilidad relativa de D y Z.



I

Se analizó el efecto de complejación sobre las propiedades espectroscópicas del cromóforo en acetonitrilo. Los resultados muestran que en presencia de los metales, se produce un incremento del coeficiente de extinción molar y un corrimiento al rojo de la transición π-π^*, mientras que la transición n-π^* muestra un corrimiento al azul y un aparente desdoblamiento de la banda de absorción. Las constantes de complejación fueron determinadas utilizando los cambios observados en los espectros de absorción con el agregado de las sales. La cinética de reacción del zwitterión (Z) intermediario en la fotoquímica de **I** fue estudiada usando la técnica de láser flash fotólisis en ausencia y presencia de metales. En acetonitrilo, la presencia de metales inhibe parcialmente la formación de Z y disminuye considerablemente su tiempo de vida. Estos resultados serán corroborados con un estudio del efecto de las sales sobre la distribución de fotoproductos.

P84

PHOTOPHYSICAL PROPERTIES OF P-SUBSTITUTED ANILINES

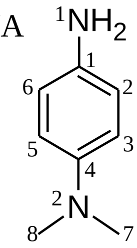
Robson Valentim Pereira and Antonio Carlos Borin*

*Instituto de Química, USP, Av. Prof. Lineu Prestes 748, 05508-900, São Paulo,
SP, Brasil, e-mail: rpereira@iq.usp.br and ancborin@iq.usp.br

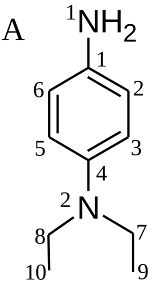
Key Words: p-substituted anilines, photophysics, computational methods

In this work, we present theoretical and experimental results on the photophysical properties of p-aminodimethylaniline (ADMA), p-aminodiethylaniline (ADEA) and p-piperidinoaniline (PA), based on geometric parameters and the electron donor properties of p-substituted groups in aniline. These results, which are the initial steps of a long term project, were obtained using *ab initio* methods with large atomic basis and the results are in agreement with the experimental electronic spectra.

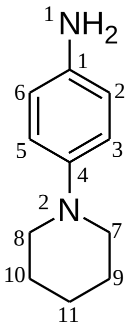
ADMA



ADEA



PA



The optimized ground states of these molecules were obtained at the CASSCF level of theory, using a DZP quality basis set. The results show that the bond distances between C(4) – N(2) are 1.415, 1.402, and 1.429Å for ADMA, ADEA, and PA respectively. The twist angle θ (defined as C(3)+C(4)+N(2)+C(7) + C(5)+C(4)+N(2)+C(8) / 2) for PA is 90^{o} as compared to $0.14\ ^{o}$ and 0^{o} for ADMA and ADEA, respectively. These data corroborate that the piperidine group in PA is less coupled to the aromatic ring.

The photophysical parameters, such as vertical excitation, and fluorescence energies were obtained at the CASSCF and CASPT2 levels, using VDZP basis set. The $S_0 – S_1$ and $S_0 – S_2$ calculated (CASPT2) and experimental (in parenthesis) values are: 323 nm (318 nm) and 256 nm (265 nm) for ADMA, 338 nm (323 nm) and 268 nm (266 nm) for ADEA, and 302 nm (310 nm) and 341nm (264 nm) for PA. These results corroborate the data from optimized structures, indicating a less strong interaction between the piperidine group and the aromatic ring. Therefore, the electron donor strength in PA is smaller than ADMA and ADEA.

Acknowledgement: The authors thank CNPq and FAPESP for financial support.

P85

CORRELACIÓN ENTRE PROPIEDADES ÁCIDO- BASE DE COMPUESTOS HETEROCÍCLICOS NITROGENADOS Y SU COMPORTAMIENTO COMO MATRICES UV-MALDI MS

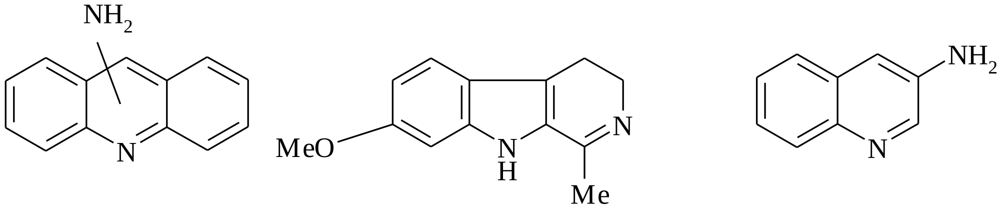
Gabriela Petroselli y Rosa Erra-Balsells

CIHIDECAR-CONICET, Dpto. de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, 3º Piso, Pabellón 2, Ciudad Universitaria, 1428 Buenos Aires, Argentina. gpetroselli@qo.fcen.uba.ar, erra@qo.fcen.uba.ar

Palabras clave: matrices UV-MALDI MS, estabilidad fotoquímica

La espectroscopía de masa con volatilización (desorción)/ionización fotosensibilizada por una matriz e inducida por láser ultravioleta (UV- MALDI-MS) es una técnica utilizada para el análisis de macro y biomoléculas. La falta de un modelo que explique claramente el proceso que ocurre en la muestra sólida formada por la matriz (fotosensibilizador) y el analito, limita fuertemente el uso de esta técnica, ya que dado un analito, es difícil la selección de la matriz adecuada.[1] Al elegir una matriz debe considerase: a) que la matriz absorba intensamente a la longitud de onda de irradiación , b) que la interacción matriz-analito lleve a una muestra homogénea y c) que las propiedades ácido-base de la matriz promuevan la formación de iones moleculares del análito.

En este trabajo se describe el análisis por UV-MALDI-MS de lípidos utilizando como matrices compuestos heterocíclicos nitrogenados (Figura 1). Entre ellos se encuentran la harmalina, una β-carbolina que presenta un equilibrio ácido-base en solución acuosa debido a la protonación del nitrógeno piridínico cuyo pKa es cercano a 10.[2] Para este compuesto se conoce además que en el estado excitado singlete su basicidad aumenta considerablemente.[2] Estas características la convierte en una excelente matriz en modo negativo. Respecto a los otros compuestos, no hay información en literatura acerca de la influencia del cambio de acidez en el estado excitado sobre su aplicabilidad en la técnica UV-MALDI. Considerando sus características estructurales decidimos utilizar estos heterociclos básicos como matrices para la detección de diversos lípidos comerciales y componentes naturales de extractos vegetales, evaluando la reproducibilidad y el límite de detección de estas matrices. Complementariamente, se estudió su estabilidad fotoquímica y térmica.



aminoacridinas harmalina 3 aminoquinolina

Figura 1: Estructura química de algunas de las matrices utilizadas

Referencias

[1] Knochenmuss R, Zenobi R (2003) Chem Rev 103:441-452

[2] Miriana C Biodic. Tesis Doctoral-FCENUBA 1996

P86

DEGRADATION OF AROMATIC COMPOUNDS USING TIO_2 AS HETEROGENEOUS PHOTOCATALYST 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. eduardo.pino@usach.cl, maria.encinas@usach.cl

Keywords: photocatalysis heterogeneous, chlorophenols, competitive degradation

In recent years, 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 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 free *4-chlorophenol* (4-CP) and *2,6-dichlorophenol* (2,6-DCP), and an equimolar mixture at 10^{-4} and 10^{-6} M concentrations in aqueous suspension using TiO_2 as heterogeneous photocatalytic at constant loading (0.5 gL^{-1}). The initial degradation rate was monitored using High Performance Liquid Chromatography. These studies showed that the degradation rate decreased when the CPs concentration was increased, suggesting a complex degradation kinetics. On the other hand, the degradation rate of 4-CP was faster than that of 2,6-DCP. Furthermore, the results obtained with an equimolar mixture of both studied phenols showed that the degradation rate of 4CP was similar to the free compound. However, the 2,6-DCP degradation was faster in the presence of 4-CP. These results suggest a direct reaction between an active intermediate produced in the degradation of 4-CP and the 2,6-DCP in solution[3]. Furthermore, at high concentration limit (~10^{-4}M), the kinetic profile showed the accumulation of two principal products which were eliminated to long degradation times. This behavior did not observe to low concentration of CPs. In all cases, we have observed a decrease of the pH solution; this is in agreement with the HCl generation[4].

In conclusion our results evidence that the degradation process induced by Heterogeneous Photocatalysis, using TiO_2 and UV light, of equimolar mixture are more complex than the degradation of individual *chlorophenols. C*onsequently competitive degradation studies must be carried out to obtain a more realistic perspective.

References.

[1]*Chem. Rev.* 1995, 95, 69; [2]App. Cat. B. Enviromental 1999, 21, 1; [3]J. Photochem. Photobiol. A. Chemistry 2006, 179,256; [4]J. Photochem. Photobiol. A. Chemistry 2008, 200,421.

Acknowledgment. Financial support from the Bicentenary of Science and Technology Program, PDA-03.

P87

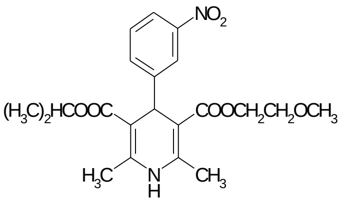
PHOTOCHEMICAL DEGRADATION OF FELODIPINE AND NIMODIPINE IN MICELLES AND LIPOSOMES

Nancy Pizarro, **Julio Brito, Andrés Pozo**

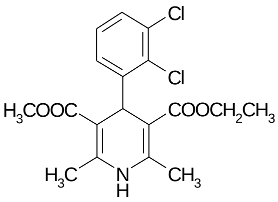
Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales,
Universidad Andrés Bello, Santiago, Chile, Av. República 275.
E-mail: npizarro@unab.cl

Keywords: photodegradation, 1,4-dihydropyridines, medium effect

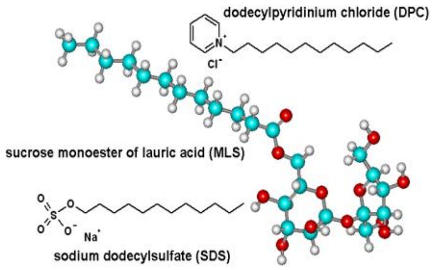
Photochemistry in organized microheterogeneous media can differ markedly from that in any homogeneous fluid medium. Additionally, they are a useful tool to mimic the extremely efficient chemical processes in the biological systems. Nimodipine and felodipine are drugs widely used as antihypertensive calcium channel blockers. Unfortunately, they are photolabile and have been related to skin photodamage.[i, ii] In a previous study we have analyzed the photophysics and photochemistry of nimodipine and felodipine in homogeneous media,[iii] here we revise the behavior of these drugs in constrained media. Specifically, we focused this work on the kinetic analysis of 1,4-dihydropyridine photodegradation process when they are incorporated into biological-mimicking systems like micelles or liposomes. As the nature of the head of surfactant (ionic or nonionic) could be important to modulate the photo-reactivity of these drugs, we studied the photodegradation of nimodipine and felodipine incorporated to micelles formed with different kind of surfactants like sodium dodecyl sulfate micelles (SDS, anionic), dodecyl-pyridinium chloride micelles (DPC, cationic) and mono lauryl sucrose ester micelles (MLS, nonionic). For comparison, the results of the photodegradation of these compounds in liposomes were also included. We have found kinetic constants in the order of 10^{-2} min^{-1} for the photodegradation of nimodipine in these microheterogeneous systems while an order of 10^{-1} min^{-1} was evaluated when benzene or ethanol were used as homogeneous solvent. In all the media explored, the rate of photodecomposition of nimodipine was higher than that for felodipine. The results clearly indicate that both dihydropyridines studied (nimodipine and felodipine) could be located near to the interface, thus the different heads of surfactants affect the rate constant in a fair (slight) different way.



Nimodipine



Felodipine



Surfactants

Acknowledgements: This work was supported by Project UNAB_DI_32_10R.

References:

i J. Ferguson. Photodermatol. Photoimmunol. Photomed. 2002, 18, 262-269.

ii J.F. Silvestre, M.P. Albares, L. Carnero and R. Botella. J. Am. Acad. Dermatol. 2001, 45, 323-324.

iii N. Pizarro, G. Günther and L. J. Nuñez-Vergara, J. Photochem. Photobiol. A, 2007, 189, 23-29.

P88

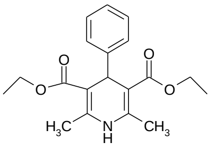
PHOTOPHYSICAL AND PHOTOCHEMICAL BEHAVIOUR OF 4-(*p*-HYDROXYPHENYL)-1,4-DIHYDROPYRIDINE

Nancy Pizarro[*], **Karina Cabezas**[*], **Luis Núñez-Vergara**[#]

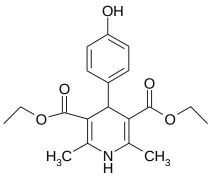
* Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales,
Universidad Andrés Bello, Santiago, Chile, Av. República 275. e-mail: npizarro@unab.cl
\# Departamento de Farmacología y Toxicol., Facultad de Ciencias Químicas y Farm.,
Universidad de Chile, Casilla 233, Santiago, Chile.

Keywords: photochemistry, 1,4-dihydropyridine, electron-donor substituent

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]
Taking into account that almost all generations of antihypertensive drugs (commercial compounds) have electron-withdrawing substituents on 4-aryl moiety, we replaced them for an electron-donor group (e.g. hydroxy) in order to modify their photophysical and photochemical behaviour. Thus, the present work has been focused on the kinetic analysis of photodegradation process of compounds **A** and **B**, identifying main photoproducts, its ability to generate singlet oxygen and its reactivity toward this active species of oxygen. The kinetic constant values of A and B photodecomposition were lower than that of their analogues 4-(3-nitrophenyl) and 4-(2,3-dichlorophenyl) substituted. On the other hand, 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

Acknowledgements: This work was supported by Project UNAB_DI_32_10R.

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.

P89

PHOTOCHEMISTRY OF 2-(2'-NITROPHENYL)-5,5-DIMETHYL-1,3-DIOXANE AND 2-(2'-NITROPHENYL)-1,3-DITHIANE.

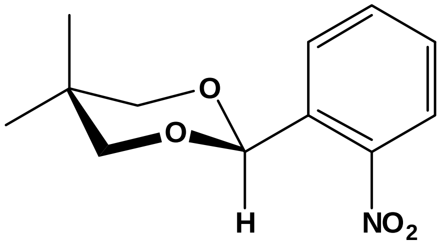
Nancy Pizarro, Evelyn Espinoza, Carlos A. Escobar

Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales,
Universidad Andrés Bello, Santiago, Chile, Av. República 275.
e-mail: npizarro@unab.cl

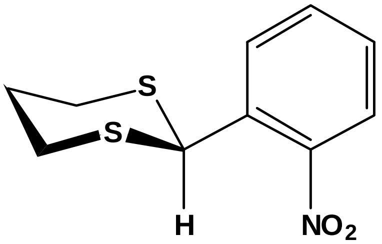
Keywords: photochemistry, 2-nitrophenyl derivatives, photoreduction

2,2-Dimethyl-1,3-propanediol and 1,3-dithiane are common aldehyde protecting groups. They are used to protect 2-nitrobenzaldehyde affording 1,3-dioxane heterocycle (i.e. A) and 1,3-dithiane heterocycle (i.e. B). These can be removed in acid media and also react photochemically through a well-known mechanism called aci-nitro tautomerism.[1,2] In this last context, the heterocycle-opening is obtained as photoproduct, additionally, the photoreduction of nitro to nitroso group is observed.

We focused this work on the kinetic analysis of photodegradation process of compounds **A** and **B** in different media, identifying also the main photoproducts. The photodecomposition kinetic constant values of **A** and **B** were very high, in the order of 10^{-3} s^{-1}. The steric and stereoelectronic contributions of both dioxo and dithio protecting groups seem to have any effect over the rate of photoreduction of these 2-nitrophenyl derivatives in solvents of different polarities.



A



B

Acknowledgements: This work was supported by Fondecyt through Grant No 1080147 and Project UNAB_DI_32_10R.

References:

1.- A. Kostikov and V. Popik. Organic Letters, 2008, 10(22) 5277-5280.
2.- P. Sebej, T. Solomek, L. Hroudna, P. Brancova and P. Klan. J. Org. Chem. 2009, 74, 8647-8658.

P90

PHOTOSTABILIZATION OF 1,5-BENZODIAZEPINES INDUCED BY ACETYLATION.

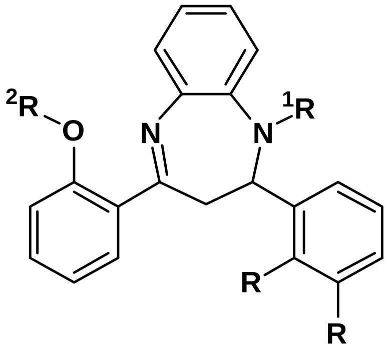
Nancy Pizarro, Francisco González, Héctor Gallardo, Carlos A. Escobar

Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales,
Universidad Andrés Bello, Santiago, Chile, Av. República 275.
e-mail: npizarro@unab.cl

Keywords: photochemistry, 1,5-benzodiazepines, N and O-acetylation effect

The compounds 4-(2-hydroxyphenyl)-2-phenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (**1a**) and 4-(2-hydroxyphenyl)-2-(2,3-dimethoxyphenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine (**2a**) are able to react with acetic anhydride, affording both, the N-acetylated or the N- and O-diacetylated analogs, depending on the reaction conditions [1,2]. When Compounds **1a-c** and compounds **2a-c** are exposed to UV light, different behaviors have been observed. Compounds without acetylation (**1a, 2a**) and the N-acetylated ones (**1b, 2b**) photodecompose *ca*. ten times faster than their diacetylated homologues (**1c, 2c**). Thus, we focused the present work on the kinetic analysis of photodegradation process of this family of compounds, identifying also the main photoproducts.

Our results shows that the introduction of double acetylation (*i.e. N*- and an *O*-diacetylation) in the 2,3-dihydro-1*H*-1,5-benzodiazepine core, plays an important role in the stability of 1,5-benzodiazepine against UV light irradiation, suggesting the importance of the O-acetylation in the decomposition mechanism mediated by UV light.



(1a) R = H ; ^{1}R = H ; ^{2}R = H

(1b) R = H ; ^{1}R = $COCH_3$; ^{2}R = H

(1c) R = H ; ^{1}R = $COCH_3$; ^{2}R = $COCH_3$

(2a) R = OCH_3 ; ^{1}R = H ; ^{2}R = H

(2b) R = OCH_3 ; ^{1}R = $COCH_3$; ^{2}R = H

(2c) R = OCH_3 ; ^{1}R = $COCH_3$; ^{2}R = $COCH_3$

Acknowledgements: This work was supported by Fondecyt through Grant No 1080147 and Project UNAB_DI_32_10R.

References:

1.- C. A. Escobar, O. Donoso-Tauda, R. Araya-Maturana, D. Sicker, Synth. Comm., **2009**, *39*, 166-174.
2.- C. A. Escobar, J. Orellana-Vera, A. Vega, D. Sicker and J. Sieler., Z. Naturforsch., **2009**, 64b, 969-972.

P91

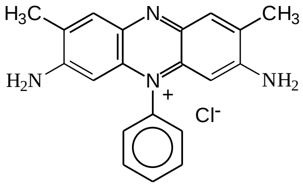
FOTOFISICA DEL COLORANTE SAFRANINA EN MICELAS INVERSAS DE AOT

Gabriela Porcal, Carlos Chesta, Sonia Bertolotti y Carlos Previtali.

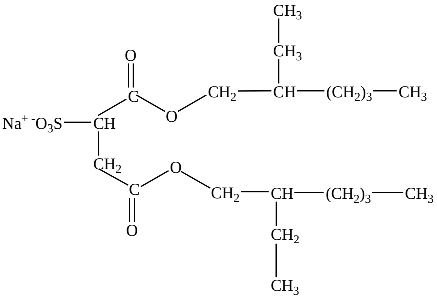
Departamento de Química, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina. email: cprevitali@exa.unrc.edu.ar

Palabras clave: colorantes, safranina, fotofísica, estado triplete, quenching.

El sistema formado por el colorante safranina (I) y aminas alifáticas se ha empleado con éxito como iniciador de la fotopolimerización vinílica. Con el fin de explorar sistemas fotoiniciadores que se puedan emplear en medios confinados hemos efectuado el estudio de la fotofísica de este colorante y la reactividad de sus estados excitados frente a aminas alifáticas en micelas inversas de AOT (II) en n-heptano. Se determinaron los espectros de absorción y de emisión del colorante en función del contenido de agua (w = $[H_2O]/[AOT]$).



(I)



(II)

El corrimiento de Stokes aumenta con w alcanzando un valor constante para w ≥ 20 el cual similar al que se encuentra en metanol pero considerablemente menor que en agua. Esto se interpreta como que el colorante (positivo) permanece en la interface (negativa) sin desplazarse a la laguna acuosa. Las propiedades del estado triplete se investigaron mediante la técnica de laser flash fotólisis. El espectro T-T presenta un máximo a 830 nm. Esto es un considerable corrimiento al rojo con respecto al agua (800 nm) y metanol (825 nm) y similar al valor en etanol (829 nm). El tiempo de vida del triplete aumenta con w alcanzando un valor límite a w > 20 considerablemte mayor que el encontrado en solventes homogéneos (60 μs en AOT y 19 μs en MeOH). Se determinó el quenching de triplete por tri-etanolamina (TEOHA), encontrándose una mayor efectividad que en solvente homogéneo: $k_q = 2.9\text{x}10^7$ en AOT contra $3.8\text{x}10^6$ $M^{-1}s^{-1}$ en MeOH. Por otra parte el quenching por tri-butil amina es mucho menos efectivo y presenta una curvatura hacia abajo similar a lo observado para aminas alifáticas en solventes homogéneo. La mayor efectividad de TEOHA se interpreta como una alta concentración local de la misma en la interface en el micro-entorno del colorante.

P92

FUNCIONALIZAÇÃO SUPERFICIAL DE FILMES DE POLIPROPILENO COM RADIAÇÃO UV, VUV OU SÍNCROTRON

Ramanathan Rajajeyaganthan, Felipe Kessler e Daniel E. Weibel*

Laboratório de Fotoquímica e Superfícies, Instituto de Química, Universidade Federal de Rio Grande do Sul, Porto Alegre, Brasil, danielw@iq.ufrgs.br

Palabras chave: Funcionalização, Polipropileno, radiação electromagnetica

Polipropileno (PP) é um polímero termoplástico produzido pela indústria em quantidades muito grandes e com amplas aplicações. O êxito do PP baseia-se nas suas excelentes propriedades mecânicas, facilidade de moldagem e baixos custos de produção. Porém, em geral suas propriedades superficiais devem ser modificadas para uma determinada aplicação utilizando técnicas químicas e especialmente, tratamentos com plasma. O principal problema é que os filmes de PP tratados recuperam as condições iniciais hidrofóbicas em poucas horas. Outra forma de modificar a superfície do PP é a utilização de radiação eletromagnética. Na presente contribuição serão apresentados os resultado de modificação superficial de PP utilizando radiação UV, VUV ou síncrotron (SR).

Filmes finos de PP (MW= 100000, Braskem, Brasil) foram preparados pela técnica de *spin-coating* sobre substratos de aço inoxidável a partir de soluções de PP em Xileno (~ 10^{-4} M) a 125 °C. A funcionalização UV foi realizada utilizando lâmpadas de Hg de média pressão (250 ou 400 W) [1]. Uma lâmpada de Deutério quase monocromática de 140 W foi empregada com fonte de irradiação VUV. As experiências com radiação SR monocromática foram realizadas no LNLS, Campinas, Brasil na linha de luz SGM de espectroscopia VUV e Raios-X moles [2]. As superfícies modificadas de PP foram analisadas por: ângulo de contacto de água (WCA), FTIR-ATR, XPS, NEXAFS e SEM.

Quando filmes hidrofóbicos de PP (WCA ~ 110°) foram irradiados com UV na presença de soluções concentradas de H_2O_2 ou vapores de ácido acrílico (AA), o WCA diminuiu para ~ 70 e ~ 47° respectivamente após uma hora de tratamento. Ao irradiar os filmes de PP com radiação VUV em presença de ar obteve-se um WCA de ~ 65° durante o mesmo período de iluminação. Finalmente quando SR foi utilizada para irradiar superfícies de PP em combinação com uma atmosfera de oxigênio, o WCA diminuiu para ~ 60°. Medidas de FTIR-ATR, XPS e NEXAFS permitiram conferir a presença de grupos eletronegativos (OH, C=O, e COO) na superfície do PP após os tratamentos.

O grau de hidrofilicidade obtida nos filmes de PP foi extremadamente estável após os tratamentos, por exemplo, depois de 10 meses de tratamento VUV o WCA permaneceu constante em ~ 65°. Quando o tratamento foi de UV na presença de AA, o WCA também permaneceu invariante após meses do tratamento. Esse tipo de modificação permanente é de grande importância prática e contrasta com tratamentos tradicionais de plasma. Estudos estão sendo desenvolvidos para tentar conhecer a origem desta estabilidade.

[1] D. E. Weibel, A. F. Michels, F. Horowitz, R. D. S. Cavalheiro and G. V. d. S. Mota, Thin Solid Films 517 (2009) 5489.[2] D. E. Weibel, F. Kessler and G. V. da Silva Mota, Polymer Chemistry 1 (2010) 645.

P93

REACTION OF NITROXIDE PREFLUORESCENT PROBES WITH PEROXYL AND PROTEIN DERIVED RADICALS

Jael Reyes[1], Alejandra Orrego[1], Camilo López-Alarcón[2], Alexis Aspée[1]
1 Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile.
2 Facultad de Química, Pontificia Universidad Católica de Santiago, Santiago, Chile.
email: alexis.aspee@usach.cl

Palabras clave: prefluorescent nitroxide probes, peroxyl radicals, protein radicals.

Nitroxide prefluorescent probes have been used as fluorescent molecular switches to monitor carbon center radicals.[1] The mechanism is based on the reaction of nitroxides with carbon center radicals removing the intramolecular chromophore fluorescence quenching elicited by a covalently attached nitroxide moiety. The extension of this methodology to other free radicals such as to peroxyl radicals requires a limited free radical reactivity of the chromophore in comparison with the nitroxide moeity.[2] In the present report, we evaluate the reactivity of the nitroxides quinoline TEMPO (QT) and coumarine 343 TEMPO ($C_{343}T$) toward peroxyl radicals via formation of oxoammonium cation and the oxidation of the chromophore moiety. Also, experiments were aimed to estimate if the interaction of protein derived radicals with QT and $C_{343}T$ involves the nitroxide or the chromophore. The reaction of nitroxides and the isolated chromophores towards peroxyl radicals (derived from 2,2'-azobis-2-amidino propane, AAPH), in absence and presence of proteins, was determined using spectroscopic techniques and ORAC (Oxygen Radical Absorbance Capacity) assay. These experiments showed that nitroxide and also chromophore moieties of QT and $C_{343}T$ reacted efficiently towards peroxyl radicals. In contrast, in presence of micromolar concentrations of lysozyme, alkaline phosphatase or alcohol dehydrogenase only the nitroxide moiety was consumed by free radicals (observed by a clear increase of the probe fluorescence). This result is in agreement with trapping of protein free radicals by nitroxide probes in conditions where AAPH derived peroxyl radical were trapped by the proteins (zero order). In these systems, no association of the nitroxide to these proteins by fluorescence time resolved techniques was observed. On the other hand, in presence of human serum albumin (HSA) a faster fluorescence increasing of QT and $C_{343}T$ is interpreted in terms of preferential association of the probes in site I in HSA,[3] and also to nitroxide trapping of thyl radicals in addition to Tyr and or Trp derived radicals.

Acknowledgments: Financial support from FONDECYT 1085177. A. O. thanks to CONICYT Doctoral fellowship.

3. Aspée. A., García, O., Maretti, L., Sastre, R., Scaiano, J. C. *Macromolecules*, 2003, **36**, 3550; Coenjarts, C., García, O., Llauger, L., Palfreyman, J., Vinette, A., Scaiano, J. C. *J. Am. Chem. Soc.* 2003, **125**, 620.
4. Jia, M., Tang, Y, Lam, Y-F., Green, S. A., Blough, N. V. *Anal.Chem.* 2009, **81**, 8033.
5. Aspée, A., Orrego, A., Alarcón, E., López-Alarcón, C., Poblete, H., Gonzalez-Nilo, D. *Bioorg. Med. Chem. Letts*. 2009, **19**, 6382.

P94

SYNTHESIS AND PHOTODYNAMIC ACTIVITY EVALUATION OF THE HYPERICIN

Anderson O. Ribeiro[*], Kleber T. de Oliveira[*], Cláudio R. Neri[Φ], Osvaldo A. Serra[Φ], Yassuko Iamamoto[Φ], Cláudia Bernal[#], Hidetake Isamato[#], Janice R. Perussi[#].

[*]Universidade Federal do ABC, Santo André - SP, Brasil anderson.ribeiro@ufabc.edu.br
[Φ] Departamento de Química, Universidade de São Paulo, Ribeirão Preto - SP, Brasil
[#] Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos - SP, Brasil

Key words: Hypericin, Photodynamic Therapy, Photosensitizers

Photodynamic therapy (PDT) is an important developed technology for cancer treatment and microorganisms inactivation. This technique is based on the production of reactive oxygen species by visible light excitation of a photosensitizer. Hypericin (HY), a pigment found in plants of the Hypericum genus, has been considered as a potential photodynamic agent [1]. Some studies have demonstrated the efficacy of topical Hypericin-PDT treatments of actinic keratosis, for example. In this work, are described one adapted synthetical route in order to obtain this anthraquinone-derivative, and its photodynamic activity was compared to some commercial photosensitizers.

Firstly, 6-methyl-1,3,8-trihydroxy-anthraquinone (emodin) was dissolved in acetic acid and reducedby using $SnCl_2.2H_2O/HCl$ [2]. After refluxing for 3 h, emodin-anthrone was precipitated by cooling at roomtemperature and the product was filtered off. Then, a mixture of emodin-anthrone, potassium t-butoxide anddimethylformamide (DMF) was irradiated by using microwave at 150W under nitrogen atmosphere, for 20 min. After cooling, the mixture was quenched with deionized H_2O and acidified with 2.0 mol.L^{-1} HCl. The residue was centrifuged and purified by column chromatography yielding protohypericin. This compound was irradiated in acetone by using halogen lamp (500 W) in order to produce Hypericin (HY).

The phototoxicity investigation of HY was performed in two tumor cell lines: HEp-2 (human larynx) and B16F12 (human melanoma). In order to compare its photodynamic efficiency, two other first and second-generation photosensitizers were evaluated at the same conditions, being respectively an hematoporphyrin derivative (Photogem®- PG) and a chlorine derivative (Photodithazine®- PZ). For HEp-2 cells the IC_{50} were 0.06 (HY), 1.0 (PZ) and 4.3 (PG), showing that HY is 94 and 99% more cytotoxic than the chlorin and the porphyrin, respectively. In B16F12 the IC_{50} values were 0.30 (HY), 3.0 (PZ) and 11 (PG), showing that HY is 90 and 97% more cytotoxic than the chlorine and the porphyrin, respectively. It can be observed that melanoma cells are more resistant to PDT since the IC_{50} is higher in this cell line for all studied photosensitizers (5; 3 and 2.5 fold for HY, PZ and PG). These results and the fact that HY is a popular and safe medicine for humans, support the great potential of this photosensitizer to replace with advantages the porphyrins as the most used photosensitizer in clinical PDT.

[1] Aigner, S., Falk, H. Monatsh Chem 2008, 139, 991.;
[2] Kiesslich, T., Krammer, B., Plaetzer, K., Curr. Med. Chem. 2006, 13, 2189.

P95

PHOTOCHEMICAL AND PHOTOPHYSICAL STUDIES AND THEORETICAL CALCULATION OF THE COMPLEX *cis*-[Ru(phen)$_2$(hist)$_2$](PF$_6$)$_2$

Carolina Riverin Cardoso[*], **Rose Maria Carlos**[*]

[*] Departamento de Química, Universidade Federal de São Carlos, São Carlos, Brasil,
carolinariverin@yahoo.com.br

Palavras Chaves: Ruthenium complexes, Photochemistry and theoretical calculation

Histamine (hist) has been broadly established as having important roles in mammalian physiology, for example, as a bioregulatory agent in vasodilation and neuronal signaling. Moreover histamine has shown encouraging anti-tumor and anti-metastatic properties and implications for Alzheimer's disease therapy. Unfortunately, the limiting factor is the hist intolerance. In this context, metal-hist complexes can be seen as useful delivery agents of hist and, in particular, are promising for the photochemical delivery of hist to desired physiological targets.

The complex *cis*-[Ru(phen)$_2$(hist)$_2$](PF$_6$)$_2$ (Ru-hist) has been synthesized and characterized and its behavior upon irradiation has been studied by continuous photolysis. The ^{1}H NMR spectrum revealed the presence of 4 peaks due to the ring protons of imidazole and 4 peaks due to the CH$_2$ group. The two sets of resonance doublet signals indicate the presence of two isomers of complex Ru-hist, the adjacent (**A)** and remote (**R)** isomer, depending on which nitrogen atom of imidazole is coordinated to the ruthenium ion. The structures of the two isomers of complex Ru-hist were further confirmed by DFT calculations.

The photochemical behavior of isomeric forms of complex Ru-hist was provided by examining the ^{1}H NMR in a CD$_3$CN and CD$_3$OD solvent. The ^{1}H NMR spectra after 30 min irradiation the **R** isomer has photochemistry while the **A** isomer remain intact.

Photolysis was also accompanied by changes in the emission spectra. In this experiment the emission intensity in CH$_3$CN solution decreased continuously during photolysis. In accordance, the *cis*-[Ru(phen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ complex shows no luminescence at room temperature.

Overall, these results are of particular interest to the design of intelligent metallodrugs based on photochemical and photophysical processes.

P96

QUANTUM-MECHANICAL ESTIMATE OF FIRST HYPERPOLARIZABILITY AND SPECTROSCOPIC PARAMETERS OF ZINC PHTHALOCYANINE DERIVATIVES

Weverson Rodrigues Gomes, Diesley Martins da Silva Araújo and Antonio Eduardo da Hora Machado

Universidade Federal de Uberlândia, Instituto de Química/Laboratório de Fotoquímica
Av. João Naves de Ávila, 2121; 38408-100 Uberlândia, MG, Brazil, e-mail:
weverson_rodrigues@yahoo.com.br, diesleymartins@yahoo.com.br, aeduardo@ufu.br

Keywords: Zinc phthalocyanine derivatives, spectroscopic and non-linear optical parameters, quantum mechanics.

This communication deals about the use of molecular design based on quantum mechanical calculation to support the synthesis of new metal-phthalocyanine derivatives aiming technological applications, such as photonics, energy conversion, photosensitization and catalysis/photocatalysis.

The ground state geometry of Zinc Phthalocyanine (ZnPc) and Tetra (α and β) nitro, amino, methoxy and dimethylamino ZnPc was optimized using the Density Functional Theory (DFT) procedure based on the B3LYP hybrid functional, without any symmetry constraints, using the DGDZVP2 valence double-ζ 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 optimized geometries were also used to estimate the polarizability (α) and the first hyperpolarizability (β) of these molecules obtained by single point calculations applying the PM6 semi-empirical model, in combination with COSMO (conductor-like screening model), using the APOLAR approach in combination with Configuration Interaction calculation. Also from the optimized structures, the excitation, fluorescence spectra and the state diagram (singlet and triplet) were simulated using TD-DFT and the same SCRF procedure. The theoretical data confirm the trend experimentally observed, showing that the electron-donor substituents favours the batochromic shift of the Q band, formed by two degenerate states. The first two triplet states also show to be degenerate and energetically adjacent to the S_1 and S_2 states. The S-T energy gap systematically decreases with the inclusion of substituents on ZnPc, being that this decrease is slightly higher for electron-donor derivatives with substitution at the α position. The parameters polarizability and first hyperpolarizability are very expressive and tend to increase as the electron donor character of the α and β substituents increases. The substituents at the α position possessing donor character present the highest values of these two parameters. These effects are probably related to the improvement in the electronic delocalization over the π system and structural distortions caused by the substituent at the α position.

Acknowledgements. To CNPq, CAPES and FAPEMIG.

P97

PHOTOELECTRIC BEHAVIOR OF HYDROXOALUMINIUMTRICARBOXY-MONOAMIDE PHTHALOCYANINE ADSORBED ON TiO_2

Hernán B. Rodríguez,* **Yésica Di Iorio**[#], **Marta I. Litter**[§], **María A. Grela**[#] **and Enrique San Román***

* INQUIMAE/DQIAyQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. II, 1428 Ciudad de Buenos Aires, Argentina.
e-mail: hbr@qi.fcen.uba.ar
[#] Departamento de Química, Universidad Nacional de Mar del Plata, Funes 3350, 7602 Mar del Plata, Argentina.
[§] Gerencia Química, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, 1650 San Martín, Prov. de Buenos Aires, Argentina.

Keywords: AlTCPc, TiO_2, action spectrum

Recently, we have tested the capability of hydroxoaluminiumtricarboxymonoamide phthalocyanine (AlTCPc) adsorbed on TiO_2 Degussa P-25 for the photocatalytic reduction of Cr(VI) under visible irradiation in the presence of 4-chlorophenol as sacrificial electron donor.[1] It was demonstrated that a very rapid reduction to Cr(III) is possible in spite of the aggregation of AlTCPc on the surface of TiO_2. In order to elucidate the role of aggregates in charge injection, the photoelectric behavior of AlTCPc adsorbed on a TiO_2 electrode is studied in this work.

Nanocrystalline TiO_2 electrodes were prepared from Degussa P-25. The powder was milled with a small amount of water and acetylacetone for a long time in order to lower the degree of aggregation and stabilized with Tween 80. Films were obtained extending the white viscous paste over ITO electrodes, drying at 100 ºC for 1 h and heating at 500 ºC for 30 min. AlTCPc was adsorbed onto the modified electrodes from dimethylsulfoxide (DMSO) and characterized through total reflectance and diffuse transmittance measurements to obtain the absorption spectrum. The circuit was closed using a SnO_2-graphite counter-electrode and a thin layer of 0.5 M KI – 0.05 M I_2 in ethyleneglycol as the electrolyte. Photocurrents were measured either directly or using modulation techniques under irradiation in the red (AlTCPc Q-band) as a function of the applied potential and dye loading.

Absorption spectra do not depend on dye loading and suggest a high aggregation degree as found in Degussa P-25 suspensions,[1] whereas photocurrent spectra do not depend on the applied potential and dye loading and resemble the absorption spectrum of the monomeric dye in DMSO. These results show that the species responsible for the charge injection is the monomeric AlTCPc. Slow response times ($\tau \sim 0.6$ s) and a large increase of photocurrent on electrodes previously illuminated at open circuit for different time intervals are observed. The origin of the photoelectric response is analyzed and discussed.

---

[1] J. M. Meichtry, V. Rivera, Y. Di Iorio, H. B. Rodríguez, E. San Román, M. A. Grela and M. I. Litter (2009) *Photochem. Photobiol. Sci.* **8**: 604-612.

P98

PHOTOLYSIS OF COMPLEXES *cis*-[Ru(N^N)$_2$(Apy)$_2$](PF$_6$)$_2$: POTENTIAL USE IN THE TREATMENT OF NEUROLOGICAL DISEASES

Mariana Romano Camilo[1#] **and Rose Maria Carlos**[1*]

[1] Departamento de Química, Universidade Federal de São Carlos (UFSCar), Caixa
Postal 676, 13565-905 São Carlos/SP, Brazil
[#] marianarcamilo@dq.ufscar.br; *rosem@ufscar.br

Keywords: Ruthenium(II), aminopyridine and DFT

Aminopyridines (Apy) are bioactive molecule that increases the strength of the nerve signal[1]. Due to it ability to facilitate nerve transmission, they has been applied to reverse anesthesia and muscle relaxation and have been propose as drug for a series of neurological diseases[2]. Temporally and spatially controlled release of biologically active molecules can be achieved with suitable photolabile precursors metal complexes[3]. In this respect, research in this lab is concerned with applying photochemical and photophysical techniques to map the chemical reactivity of Ru(II) complexes as potential Apy donors. Here is described the synthesis, characterization, theoretical calculations and photochemical properties of a series of *cis*-[Ru^{II}(**N^N**)$_2$(Apy)$_2$]$^{2+}$ complexes [(**N^N**) = 1,10-phenanthroline].

The complexes {Ru(II)-neuroactive} were obtained from precursor *cis*-[Ru(**N^N**)$_2$(OH$_2$)$_2$]$^{2+}$ after an amount of the Apy ligand added and were precipitated with NH$_4$PF$_6$. Photochemical studies of complexes using spectroscopic technique (UV-vis) were made to prove the spectra and dynamics of photoproducts and possible reactive intermediates. The complexes show lowest energy absorption at 490 nm ($\varepsilon \sim 10^4$ M^{-1} cm^{-1}) in CH$_3$CN solution corresponding to the MLCT (Ru→phen and Ru→Apy, both $d\pi \rightarrow \pi^*$). Based on Density Functional Theory (DFT) calculations using the Gaussian 03 program (B3LYP exchange-correlation functional with the LANL2DZ basis set) the electronic spectra of both complexes were investigated in CH$_3$CN: λ = 485 nm; 441 nm (f = 0.080; 0.085). Upon photolysis in CH$_3$CN with 420 and 350 nm light, the complexes undergo Apy dissociation to give the ruthenium(II) solvent products detected by UV-vis absorption: the absorbance of MLCT band at 490 nm (λ_{max}) decreases during the photolysis and a band at λ_{max} = 420 nm, characteristic of complex solvent *cis*-[Ru^{II}(**N^N**)$_2$(CH$_3$CN)$_2$]$^{2+}$, appears. The photochemical results are relevant to possible applications of photochemistry for Apy delivery to biological targets.

Financial support: FAPESP

[1] Molgo, J; Lemeignan, M.; Peradejordi, F.; Lechat, P.; *J. Pharmacol* (Paris), **1985**, 16, 109-144.
[2] Segal, J. L.; Brunnemann, S. R.; *Pharmacotherapy*, **1997**, 17, 415-423.
[3] Carlos, R. M.; *Quim. Nova, **2007**,* Vol. 30, No. 7, 1686-1694.

P99

ESTUDIO EXPERIMENTAL Y TEÓRICO DE LAS ESPECIES TRANSIENTES OBTENIDAS POR FLASH-FOTÓLISIS DE ÁCIDOS FÚLVICOS.

Janina A. Rosso* , Mónica C. Gonzalez* , Reinaldo Pis Diez#, Daniel O. Mártire*

* 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: dmartire@inifta.unlp.edu.ar.
# Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Facultad de Ciencias Exactas, Universidad Nacional de la Plata, (1900) La Plata, Argentina.

Palabras clave: ácidos fúlvicos, radical catión, flash-fotólisis.

Las sustancias húmicas SH son las sustancias que más absorben la luz solar en las aguas naturales. A partir del proceso de absorción de luz UV-visible se generan estados excitados que interaccionan con especies presentes en el agua formando otros intermediarios reactivos, afectando la química redox de estas aguas y la de los contaminantes que se encuentran disueltos en ellas. Los ácidos fúlvicos (AF) corresponden a la fracción de las SH que es soluble en soluciones acuosas a cualquier valor de pH.

En este trabajo se realizaron experimentos de láser flash-fotólisis (LFP) con soluciones ácidas de AF Pony Lake y Waskish Peat (ambos de IHSS). Los espectros de absorción de las especies transientes obtenidas se muestran en la Figura 1.

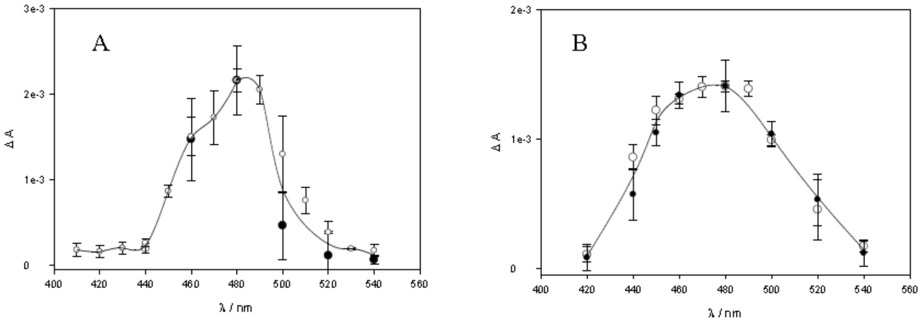


Figura 1: Espectros de absorción de los transientes obtenidos por LFP (λexc=355 nm) con soluciones de AF Pony Lake 188 mgL^{-1} (A) y Waskish Peat 98 mgL^{-1}(B) de pH = 1,8 burbujeadas en Ar (○) y O_2 (●).

Tanto los espectros de absorción como las cinéticas de decaimiento fueron independientes de [O_2]. Estos resultados indicarían que las especies transiente detectadas podrían asignarse a radicales cationes de los AF.

Como complemento del trabajo experimental, se estudiaron el estado fundamental y los primeros estados excitados de los estados triplete y radical catión del modelo de Buffle. Se utilizaron herramientas de la teoría del funcional de la densidad que incluyen efecto solvente.

Los resultados preliminares soportan los datos experimentales, sugiriendo que la transición observada ocurre entre el estado fundamental y el segundo estado excitado del radical catión de la especie en estudio.

P100

PHOTOINDUCED POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE USING AS PHOTOINITIATOR SAFRANINE DYE AND AMINE GROUPS INCORPORATED IN A DENDRIMER.

Ana María Rufs*, María Victoria Encinas*, Carlos Previtali#, Sonia Bertolotti#

* Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile, e-mail: maria.encinas@usach.cl.
# Departamento de Química, Universidad Nacional de Río Cuarto, Río Cuarto, Argentina.

Keywords: Safranine, dendrimers, branched polymers.

The synthesis of polymers with complex architecture has been of wide interest, in particular that concerning to branched polymers. Among the methods to obtain these materials from vinyl monomers is the use of multifunctional initiators. However, there are few reported studies using this technique and most of them are focused to thermal free radical polymerization of styrene and methyl methacrylate.

In the present work we studied the free radical polymerization of 2-hydroxyethyl methacrylate induced by irradiation. With the aim to obtain branched polymers we employed as photoinitiator safranine (Sf) in the presence of amine groups incorporated to PAMAM dendrimers of low generation. The interaction of the dye excited triplet state with amines gives the α-amino radical that is the species that add to the monomer double bond.[1]

In order to get information of dendrimer-branched polymers, the polymerization rates were compared with the photochemical behavior of safranine in the presence of dendrimers. The characterization of polymers employing different techniques, intrinsic viscosity of the polymer solutions, particle size, and size-exclusion chromatography indicate the formation of branched polymers.

The triplet quenching of Sf by dendrimers presents a complex mechanism.[2] Time resolved measured showed that the interaction of the safranine protonated triplet ($^3SfH^+$) with the amine involves as first step an intermediate in equilibrium with the triplet, followed by the dye deprotonation giving the neutral triplet (^3Sf). This species is deactivated by the amine giving the amine free radical that adds lead to monomer.

In spite of the higher number of amine groups in dendrimers, polymerization rates using the monomeric photoinitiator was faster. These results show that branched polymers were successfully obtained with minor changes in the polymerization rate.

References:
[1] C.M. Previtali, S.G. Bertolotti, M.G. Neumann, I.A. Pastre, A.M. Rufs, M.V. Encinas, Macromolecules, 27(1994)7454-7458. [2] C.A. Suchetti, A.I. Novaira, S.G. Bertolotti, C.M. Previtali, J. Photochem. Photobiol. A: Chem. 201**,** 69-74 (2009)

Finantial support: FONDECYT (Chile) grants # 1070123 and 7100023; and CONICET, Argentina.

P101

DEGRADACIÓN DE LIGNINA: ACCIÓN FOTOCATALIZADORA DE UN POLÍMERO CON FTALOCIANINAS DE Al^{III}

Gustavo Ruiz*, Paula Juliarena*, Mario Féliz*, Graham Lappin# y Guillermo Ferraudi#

* 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
Radiation Research Building, Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556. e-mail: ferraudi@hertz.rad.nd.edu

Palabras clave: Lignina – Ftalocianina de Al^{III} - Fotodegradación

Las ftalocianinas poseen propiedades fotoquímicas y fotofísicas de interés en distintas disciplinas [1]. En el caso de ftalocianinas metaladas, la unión covalente entre el metal y una fase polimérica ha sido usado como una forma para cambiar las propiedades físicas y químicas de los complejos [2]. Un trabajo previo, publicado recientemente, nos permitió conocer profundamente la fotofísica y fotoquímica de un nuevo polímero (de poly-etilenamida) conteniendo ftalocianinas tetrasulfonadas de Al^{III} (poly-Al^{III}Pc). Este polímero mostró, además, un comportamiento diferente al de Al^{III}Pc libre. Y se presentó evidencia espectroscópica de "fototransformación" de lignina [3]. La lignina es un biopolímero vegetal que se encuentra recubriendo el 30% de la celulosa y hemicelulosa disponible. Su estructura es, básicamente, la de un polímero de grupos fenólicos unidos en forma de red con sustituyentes de diferente naturaleza. Por lo tanto, la degradación de lignina presenta un desafío de importancia tecnológica generando, además, productos de interés industrial.

En este trabajo presentamos un estudio sistemático de degradación de lignina mediada por poly-Al^{III}Pc y la detección de fotoproductos que sugiere la destrucción de la estructura polifenólica. Se comunicará el resultado de experimentos de fotólisis continua en presencia y ausencia de O_2; en presencia y ausencia de poly-Al^{III}Pc y Al^{III}Pc; tiempo de irradiación, etc., así como el diseño de estrategias de separación e identificación de los fotoproductos. Las muestras fueron irradiadas con luz de $\lambda > 500$ nm (no absorbe lignina) y las soluciones acuosas (pH=7) posteriormente analizadas por espectroscopía UV-Vis, CG-FID y HPLC-masa.

Referencias

[1]. *Phthalocyanines: Properties and Applications*, C. C. Leznoff, A. B. P. Lever, Eds.; VCH: New York, 1989, 1993, 1996; Vols. 1-4.
[2]. S. Thomas, G. Ruiz, G. Ferraudi**,** *Macromolecules*, **2006,** 39, 6615.
[3]. G. T. Ruiz**,** G. Ferraudi , A. G. Lappin. *Journal of Photochemistry and Photobiology A: Chem.* 206, **2009,** 1-9.

P102

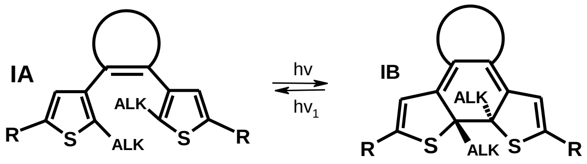
NEW ADVANCED PHOTOCHROMIC POLYMERS FOR 3D OPTICAL MEMORY

Alexey Sakharov, Mikhail Krayushkin, Valery Barachevsky[#], Valery Vasnev*, Magomed Keshtov*, Alexey Kovalev*, Alexander Rusanov*

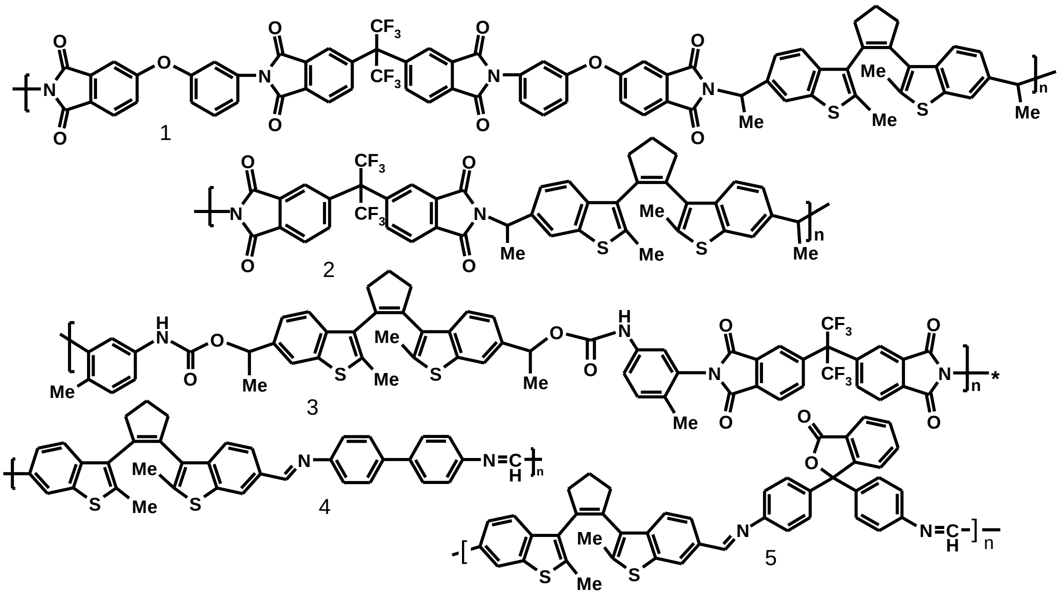
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences;
47, Leninsky prosp., 119991, Moscow, Russia, mkray@ioc.ac.ru
[#]Institution of the Russian Academy of Sciences, Photochemistry Center;
Moscow, Russia, 119421, 7a-1, Novatorov Str., barva@photonics.ru
* A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences; 28, Vavilova str. 119991, Moscow, Russia, vasnev@ineos.ac.ru

Key Words: polymers, optical memory

Dihetarylethenes I have undisputable advantage in compare with most of known photochromes, owing to their exceptional photochromic properties (thermal irreversibility of photoconversion A $\rightleftharpoons$ B, high fatigue resistance, high rate of the reaction on radiation action, high quantum yield of photocyclization) and are considered to be extremely perspective systems for the information storage in optoelectronic devices and as photoswitchers.



Methods for preparation of polymers 1-5 with dihetarylethene fragments as recording media for three-dimensional optical memory were developed.



Spectral properties of the macromolecules are discussed.

P103

SOLVENTS EFFECT ON THE PHOTOPOLYMERIZATION OF HEMA PHOTOINITIATED BY SAFRANINE O, TRIETHYLAMINE AND DIPHENYLIODONIUM CHLORIDE.

Willy G. Santos[*], Carla S. Cavalheiro[*] and Miguel G. Neumann[*]
[*] Universidade de São Paulo, São Carlos - SP, Brazil
e-mail: willy_glen@iqsc.usp.br

Keywords: Solvents effect; Photopolymerization, three components

In this present work, the polymerization of hydrophilic monomer 2-Hidroxyethyl methacrylate (HEMA) was studied by a delicate balance among the effective interaction of Safranine O (SfH^+), the Diphenyliodonium chloride (DPIC) and Triethylamine (TEA) with different solvents. The photobleaching reaction was conducted in a number of solvents with different parameters of solubility, at the same temperature (298 K). The extent of bleaching was monitored spectrophotometrically by measuring the maximum visible absorbance of dye. The results show that the solvent polarity affects the rate of the photoinduced reaction and, in addition, other factors, such as the E_T^{30} and hydrogen bonding are important. Light induced polymerization of HEMA in the presence of the photoinitiator system (Safranine O, TEA and DPIC) was conducted in an ATR-FTIR coupled with a glass fiber that illumines the support with monomer solution. After irradiation the polymer was characterized by the disappearance of the C=C monomer band, which is located in 1815 or 1635 cm^{-1}. In agreement with the influence of solvent in the radical formation by initiator, the efficiency of DPIC in the photopolymerization also presents changes when different solvent media are compared by R_p values, see Figure.

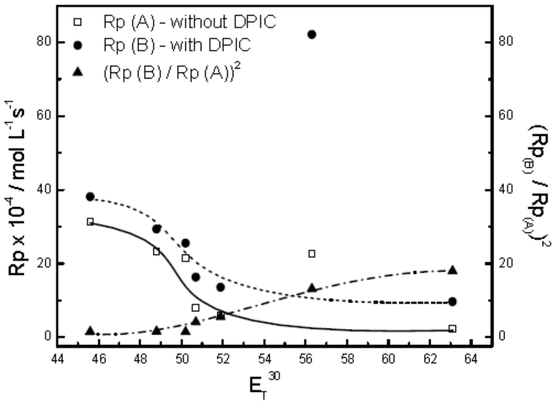
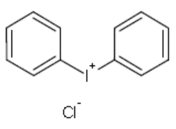
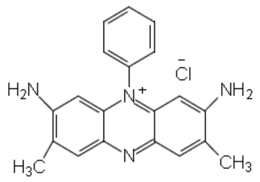


Figure. Dependence of R_p with E_T^{30} in absence (A) and presence (B) of DPIC. [$SafH^+$] = 1×10^{-5} $molL^{-1}$; [TEA] = 1×10^{-2} $molL^{-1}$; solvent/monomer ratio: 1/5.

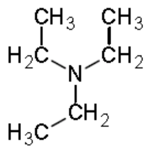
Structure of chemical components



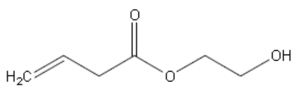
DPIC



SfH^+



TEA



HEMA

P104

Determination of Ground State Rate Constants for Proton Transfer of Two Hydroxymethyl Flavylium Salts by Nanosecond Laser Flash Photolysis

Sergio Pereira de Souza Jr.*, Barbara Mesquita Gelber*, Evan Carder$, Frank H. Quina*

*Instituto de Química, Universidade de São Paulo, São Paulo, Brazil

$Chemistry Department, University of Pittsburg, Pittsburg, USA

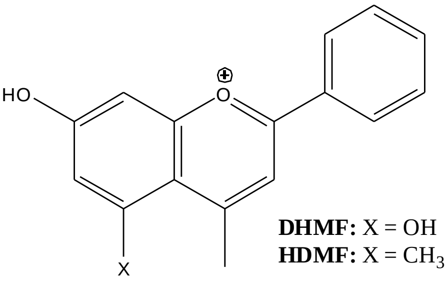
E-mail: Sergio.pereira.souza@usp.br, quina@usp.br

Key Words: Photochemistry, Flavylium Salts, Laser Flash Photolysis

Anthocyanins are plant pigments that impart most of the red, purple and blue hues in nature. The different colors reflect both the rich chemistry of these flavonoid compounds and their structural diversity, with over 600 molecular structures identified to date. The reddish colors are mainly due to the free flavylium cation form, AH^+, of anthocyanins, while the blue/purple colors are normally associated with the conjugated quinonoidal base form or with complexes of AH^+ with other polyphenols and/or metal ions. The fundamental chromophore of anthocyanins is the 7-hydroxyflavylium ion. In the ground state, the pK_as of the 7-hydroxygroup of both anthocyanins and synthetic 7-hydroxyflavylium salts are typically in the range of 4-5 in aqueous solution. In the excited state, however, 7-hydroxyflavylium ions are super-photoacids, with excited state pK_a^* values in the range of -1 to 0 and rate constants for deprotonation to water as large as 2×10^{11} s^{-1}.

In the present work we estimated proton-transfer rate constants in the ground states of two synthetic flavylium salts: 7-hydroxy-4,5-dimethylflavylium chloride **(7-HDMF)** and 5,7-dihydroxy-4-methylflavylium chloride **(5,7-DHMF)** from laser flash photolysis perturbation of the ground state equilibrium position [1]. The observed rate constants, k_{obs}, equal to the reciprocal of the lifetime, τ, of the base form of the flavylium ion, are a linear function of the hydronium ion concentration $[H^+]$: $k_{obs} = k_d + k_p[H^+]$, a plot of which provides values of k_p and k_d with the internal check of consistency $K_a = k_d/k_p$.

For both flavylium salts, deprotonation occurs at the 7-OH group in the microsecond range (3.90×10^5 and 8.9×10^5 s^{-1} for HDMF and DHMF, respectively), while reprotonation of the ground state base is essentially diffusion-controlled (2.6×10^{10} and 3.0×10^{10} s^{-1} for HDMF and DHMF, respectively).



DHMF: X = OH
HDMF: X = CH_3

References:

[1] A.L. Maçanita, P.F.Moreira Jr, J.C. Lima, F.H. Quina, C. Yihwa, C. Vautier-Giongo; J. Phys. Chem. A, **2002**, 106, 1248-1255.

Supported by: CNPq and NSF-FAPESP.

P105

REACCIONES FOTOSENSIBILIZADAS QUE AFECTAN EL LENTE OCULAR Y QUE CONTRIBUYEN AL ENVEJECIMIENTO Y LA CATARATOGENESIS.

Eduardo Silva, Felipe Ávila y Denis Fuentealba

Pontificia Universidad Católica de Chile, Facultad de Química, Departamento de
Química Física, Laboratorio de Química Biológica.
Vicuña Mackenna 4860, Santiago, Chile (e-mail: esilva@puc.cl)

Palabras clave: Fotosensibilización, radiación UVA-visible, proteínas cristalinas

El cristalino o lente ocular es un tejido constituido fundamentalmente por proteínas que poseen una tasa de recambio muy reducida, y que por lo tanto, van experimentando modificaciones químicas que se acumulan con la edad y son extremas en pacientes con catarata. La ocurrencia de entrecruzamientos proteicos debido a reacciones químicas entre los grupos carbonilos de azucares y los aminos laterales de las proteínas puede conducir a la formación de productos terminales de glicación avanzada (AGEs), los que se caracterizan por ser coloreados. En este trabajo se estudió la potencialidad como fotosensibilizadores que poseen los AGEs cuando son expuestos a la radiación en la región UVA-visible, poniendo especial énfasis en su comportamiento a baja concentración de oxígeno molecular, que es la condición que posee este tejido que no es vascularizado. Se prepararon modelos pequeños de AGEs incubando glucosa (Glc), treosa (Thr) y ascorbato (ASC) en presencia de N-acetil lisina y/o N-acetil arginina. Se obtuvieron también AGEs unidos covalentemente a las proteínas mediante la incubación de las fracciones proteicas solubles extraídas de lentes de bovino (BLP) en presencia de azúcares o ASC. Se calcularon los rendimientos cuánticos de fotodescomposición del Trp (ΦTrp) irradiando este amino ácido con luz monocromática en una atmósfera de oxígeno del 5% y en presencia de los diferentes sensibilizadores. Los valores de ΦTrp obtenidos fueron pequeños (entre 0.23×10^{-3} y $5{,}41 \times 10^{-3}$) siendo el producto de descomposición del ASC el sensibilizador más efectivo seguido por la mezcla Lys/Glc. Los diferentes cromóforos pequeños fueron también utilizados como sensibilizadores para irradiar proteínas de lente con luz UVA-visible, encontrándose la generación de entrecruzamientos proteicos acompañados de procesos oxidativos mediados por especies reactivas del oxígeno. Los rendimientos cuánticos fueron mayores cuando los experimentos se realizaron a baja concentración de oxígeno molecular y decrecen al aumentar la concentración de este al 20%, lo que indica la importancia de mecanismos de fotosensibilización de tipo I, con la generación de especies radicalarias que pueden dar cuenta de los procesos de entrecruzamiento. Cuando se irradiaron proteínas de lente coloreadas, como consecuencia de un proceso previo de glicación que se realizó en la oscuridad, se observó que estos cromóforos que están unidos covalentemente a las proteínas no son generadores de entrecruzamientos si no que producen daño fotoquímico circunscrito a la región inmediata a su localización. Se discuten los mecanismos involucrados en estas reacciones fotoquímicas.

Agradecimientos: Proyecto Puente Nº 05/2009 VRAID PUC

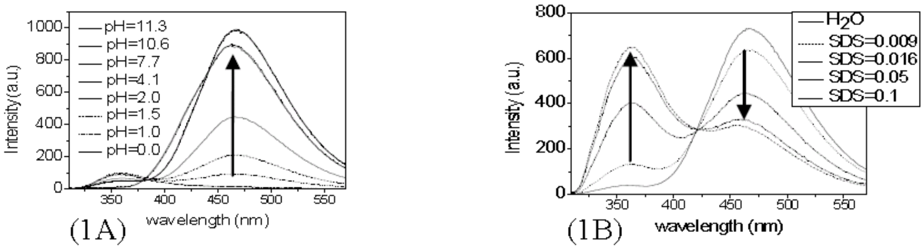
P106

PROBING THE SURFACE CHARGE OF ZWITTERIONIC AND ANIONIC MICELLES WITH FLUORESCENT PROBES

Marcelo Silva, Haidi D. Fiedler and Faruk Nome
Departamento de Química / Intituto Nacional-INCT-Catálise, Universidade Federal de
Santa Catarina, Florianópolis, SC, Brazil, Campus Universitário Trindade 88040-970,
fiedler@qmc.ufsc.br

Key Words: Micelles, SDS, Sulfobetaines.

In order to quantify the surface charge of zwitterionic and anionic micelles, 1-naphthol was used, a fluorescent probe with a large difference between the ground state pKa and the excited state pKa*.[1] The values obtained for the acid dissociation constants of the probe 1-naphthol were pKa = 10.09 ± 0.49 and pKa* = 0.085 ± 0.038, respectively. Zwitterionic sulfobetaine micelles show an effect known as "chameleon effect" which consists of strong and specific interaction with anions such as ClO^-_4. There is kinetic and electrophoretic evidence showing that such interactions cause the formation of a negative potential on the surface of the micelle, which causes transfer of H^+ from the aqueous phase to the micellar pseudophase.[2] The addition of sodium dodecyl sulfate (SDS), an anionic surfactant, in a solution containing 1-naphthol, promotes changes in the fluorescence spectrum which are consistent with formation of neutral 1-naphthol in the excited state.[3] This phenomenon is consistent with the increased concentration of H^+ in SDS micelles. To quantify the effect of different micelles, measures of fluorescence of 1-naphthol at different pH values, initially in water (Figure 1A) and in the presence of SDS (Fig. 1B) and sulfobetaines, were carried out.



(1A) (1B)

Figure 1A. Successive emission spectra of 1-naphthol in aqueous solution (λex=295nm, [1-N]=3,0 x 10^{-5}M) at different values of pH (0,0 to 11,3). **1B.** Variation in emission of 1-Naphthol (λex=295nm, [1-N]=3,0 x 10^{-5}M) depending on the concentration of SDS (0 até 0,1M), pH=7,1.

The results with 1-naphthol are consistent with those obtained with 2-naphthol as probe. However, 1-naphthol was more appropriate for determining the surface charge of SDS micelles, while for sulfobetaines 2-naphthol is more appropriate. The results indicate 0.1 M SDS promotes an apparent change of pH in the micellar phase from 7.1 to 0.6, a value which is consistent with previous studies of Selinger and Weller (1977)[3], but may well be related to significant changes in the excited state pKa values of the probes.

References

[1] Rosenberg J. L; Brinn I; **Excited State Dissociation in Naphthols**, *The Journal of Physical Chemistry*, 76, 3558, 1972.

[2] Farrukh M. A.; Beber.R C; Priebe J. P;Satnami M. L; Micke G. A; Costa A. C. O; Fiedler H.D; Bunton C.A and Nome F; **Reactivity and models for Anion Distribution: Specific Iodide Binding to Sulfobetaine Micelles**, *Langmuir*, 24, 12995, 2008.

[3] Selinger K. B; Weller A; **Excited State Acid-Base Reactions in Micelles**. *Aust. J. Chem*; 30, 2377, 1977.

P107

INTRAMOLECULAR ENERGY MIGRATION IN POLYFLUORENE ENDCAPPED WITH NAPHTHALIMIDE DERIVATIVE

Emanuelle R. Simas[1], **Jonathas P. Siqueira**[2], **Lino Misoguti**[2]
and Marcelo H. Gehlen[1]

[1] Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos-SP, Brasil.
[2]Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos-SP, Brasil.

Key words: polyfluorene, fluorescence, energy migration

In this work, poly(9,9'-di-*n*-octylfluorene) (PFO-1) and PFO-1 end-capped with N-(2-benzothiazole)-1,8-naphthalimide (PFO-2) were prepared via Ni(0) mediated Yamamoto-coupling reaction. Excited state properties of the polymers in solution were studied by time-resolved fluorescence and transient femtosecond absorption spectroscopies.

In contrast with PFO-1, fluorescence of PFO-2 is modulated by solvent polarity. Its emission spectrum at low energies has a shoulder on 540nm (Fig.1), and this fact suggests the formation of a mixed excited state configuration between the emissive singlet (fluorene units) state and the end-groups forming S-CT charge transfer state. Triexponential emission decay was found for PFO-2 (lifetimes of 26-87 ps (τ_1), 438-624 ps (τ_2) and 1-3 ns (τ_3)), in contrast with a single lifetime (τ_1=357-472 ps) fitted for PFO-1. Decay times of PFO-2 are associated with energy migration in cascade down to the mixed S-CT charge transfer state, backbone and CT emission; respectively. Time-resolved fluorescence anisotropy showed rotational relaxation time of 102-132 ps for PFO-1, ascribed to reorientation of fluorene units on polymer backbone. PFO-2, in turns, exhibited biexponential decay of anisotropy with a fast component of 7-15 ps and a slow one of 0.8-1.0 ns, showing that depolarization occurs from two processes: fast backbone energy migration to form the mixed charge transfer state and slow diffusion motion of end-segments at longer times. Results from femtosecond transient absorption measurements agree with this analysis and a fast component of about 9 ps in 603nm was only observed in PFO-2 system.

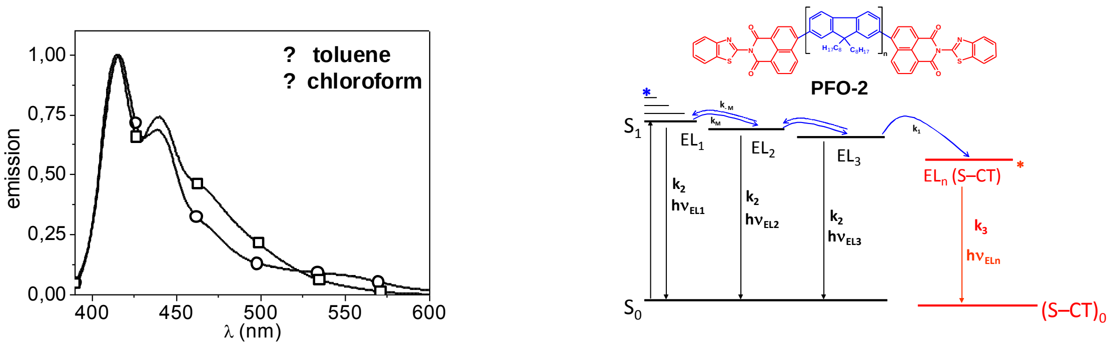


Figure 1: Emission spectra of PFO-2 in toluene (□) and chloroform (?) solutions (left). Energy diagram of the electronic states: Energy levels (EL) of PFO-2, mixed charge transfer state (S–CT), and the decay processes (k_1, k_2 and k_3) involved during emission.

P108

REACCIONES DE TRANSFERENCIA DE PROTONES EN FLUIDOS SUPERCRÍTICOS

Sabrina Simoncelli[1], Pablo A. Hoijemberg[1], M. Laura Japas[2], Pedro F. Aramendía[1]
[1] INQUIMAE y Dto. Química Inorgánica. FCEN. Universidad de Buenos Aires. [2] Gerencia Química CNEA. Buenos Aires y Universidad de General San Martín. Argentina. simoncelli@qi.fcen.uba.ar

Palabras clave: Fluorescencia, Fotoácido, Supercrítico.

La transferencia de protones es una reacción frecuente, muy común en procesos químicos (catálisis ácido-base en procesos industriales, de laboratorio o enzimáticos). La solvatación juega un papel fundamental en estas reacciones, debido a la asociada transferencia de carga.

En este trabajo se estudian la transferencia de protones en sistemas compuestos por 2-naftol y diversas aminas alifáticas en CO_2 supercrítico y en ciclohexano, usado como solvente de prueba y de referencia. El 2-naftol es un fotoácido que cambia su pKa en agua de 9,5 en el estado fundamental a 3,0 en el estado excitado singulete. Debido a que las formas básica y ácida presentan espectros diferentes de absorción y de emisión, dicha transferencia ha sido estudiado por espectroscopía de fluorescencia. Como aceptor de protones se usaron aminas alifáticas simples, con pKa menores que el pKa del fotoácido en el estado fundamental y mayores que el del fotoácido excitado. Utilizamos N-etil-diisopropilamina (DIEA); trietilamina (TEA); morfolina (M); 4-metilmorfolina (MM) y 3-dimetilamino-propionitrilo (DMP).

Se obtuvieron espectros de absorción y de fluorescencia estacionaria (emisión y excitación) en CO_2 supercrítico a diferentes temperatura y presión, desde densidades menores que la densidad crítica hasta condiciones similares a las de un líquido, y a diferentes concentraciones de amina. A bajas concentraciones de amina se observan cambios espectrales en la emisión que están relacionados con la solvatación preferencial de 2-naftol por la amina. En todos los sistemas analizados, y siempre que la concentración de la amina sea suficientemente grande, se observa transferencia de protón desde el estado fundamental de 2-naftol hacia la base. Tanto los espectros de excitación como los de emisión evidencian igual dependencia con la concentración de amina, lo que muestra que la especie que absorbe es la misma que la que emite.

Excitando en el punto isosbéstico, los cambios observados en los espectros de fluorescencia al aumentar la concentración de amina son: i) variación en el espectro de emisión de la forma ácida, dado por al efecto de solvente (solvatación preferencial); ii) disminución en la intensidad total de emisión, debida a la desactivación estática de la emisión del naftol y iii) formación de la banda de emisión del anión naftolato, originado en la transferencia de protón entre la amina y el 2-naftol.

P109

CHARACTERIZATION OF DPPC/DODAB BILAYER FRAGMENTS IN PRESENCE OF GRAMICIDIN

Marco Soto-Arriaza*, Constanza Olivares-Ortega*, Camilla de Almeida Carvalho[&] and Ana M Carmona-Ribeiro[&]
*Departamento de Química-Física, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile, Av. Vicuña Mackenna 4860, Macul, 6094411, marcosoto@uc.cl
[&] Departamento de Bioquímica, Instituto de Química, Universidade de São Paulo, São Paulo, Brasil, Av Lineu Prestes 748, Butantã, mcribeir@iq.usp.br

Key words: Bilayer Fragments, Channel Peptide, Generalized Polarization

In this work, we have characterized the physicochemical properties of bilayer fragments (BF) formed by zwitterionic phospholipid, dipalmitoylphosphatidylcholine (DPPC), and cationic lipid, dioctadecyldimethylammonium bromide (DODAB), at different proportions in absence or presence of gramicidin, a pentadecapeptide ion channel. Bilayer fragments of DPPC:DODAB were obtained in water by sonication with a macrotip above the mean phase transition temperature (Tm) of the composite bilayer. In the present work, generalized polarization of Laurdan, fluorescence anisotropy of diphenylhexatriene (DPH) and turbidity were obtained as a function of temperature to determine Tm of bilayer fragments whereas dynamic light-scattering determined mean zeta-average diameter (Dz) and zeta-potential (ς) for the dispersions. At 1:1 DPPC:DODAB, the zeta-potential (ς) for BF with 70 nm Dz was 53 ± 2 mV in contrast to 82 ±4 mV for large unilamellar vesicles about 500 nm. According to our results, for DPPC:DODAB bilayer fragments, at different mol fraction of DODAB, in absence of gramicidin, Tm decreases when % DODAB increases. The phase behavior of these bilayer fragments indicated absence of phase separation with Tm at 57.5ºC for BF with 40 mol% DODAB and Tm at 54.3ºC for BF at 60 mol%. The small reduction of Tm at high mol % of DODAB would indicate that molecular packing becomes weaker between DODAB and DPPC into bilayer fragment. On the other hand, in presence of gramicidin at 10 mol% relative to lipid content, Tm does not change at 40 mol% of DODAB, nevertheless, for DPPC:DODAB bilayer fragments at 60 mol% of DODAB, phase transition temperature increased to 57.2ºC. Thereby, samples with 60 mol% of DODAB and 10 mol% of gramicidin, molecular packing becomes tighter than the one for the DPPC:DODAB BF at the same ratio. Possibly lipid packing is less tight at the borders of the BF, giving gramicidin the opportunity to insert and tighten these less packed regions of the bilayer fragments.

Acknowledgements: This work was supported by Programa de Cooperación Científica Internacional CONICYT/CNPq 2008/212, PIFQ-2009 (MSA) and CNPq (ACR).

P110

DESACTIVACION DE LOS ESTADOS EXCITADOS DEL COLORANTE SAFANINA POR DENDRIMEROS PAMAM

Carlos Suchetti, Ana Novaira, Marcela Altamirano, Carlos Previtali y Sonia Bertolotti

Departamento de Química, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina.
email: sbertolotti@exa.unrc.edu.ar

Palabras clave: colorantes, safranina, estados excitados, dendrímeros, PAMAM, quenching

Los dendrímeros han sido utilizados en los últimos años en numerosas aplicaciones tales como liberación controlada de drogas, diversas técnicas analíticas y como macro-iniciadores de fotopolimerizaciones radicalarias[1]. Las estructuras dendríticas pueden considerarse como similares a estructuras micelares monodispersas a las cuales pueden unirse, covalentemente o por interacciones intermoleculares, diversos sustratos. Una de las estructuras dendríticas más utilizadas es el PAMAM. Estos dendrímeros, dependiendo de la generación, pueden poseer grupos aminos o carboxilicos terminales.

En trabajos anteriores del grupo hemos estudiado la interacción de los estados excitados singlete y triplete del colorante sintético safranina con las estructuras dendríticas del tipo PAMAM con grupos amino terminales,[2] con especial interés en la generación de radicales activos.

En este trabajo presentamos los resultados obtenidos con los dendrímeros de generación intermedia con grupos carboxílicos terminales. Los estudios se realizaron en agua o MeOH como solventes.

Los espectros de absorción son prácticamente insensibles a la presencia del dendrímero, mientras que se observa quenching de fluorescencia. Los gráficos de Stern Vomer en general presentan curvatura negativa, tanto para mediciones estáticas como de tiempo de vida.

La interacción con el estado triplete del colorante y la formación de especies transitorias fue investigada por la técnica de láser flash fotólisis. La cinética de desactivación del estado triplete presenta un comportamiento complejo, que parece involucrar a un equilibrio rápido de transferencia de protón en el estado excitado, seguido por una transferencia de electrón.

Referencias

[1] Xuesong Jiang, Hongjie Xu, Jie Yin, Copolymeric dendritic macrophotoinitiators. *Polymer* 46 (2005) 11079.

[2] Carlos Suchetti, Ana Novaira, Sonia Bertolotti, Carlos Previtali. The excited states interaction of safranine-O with PAMAM and DAB dendrimers in methanol. *Journal of Photochemistry and Photobiology A: Chemistry* 201 (2009) 69–74.

P111

EFFECT OF HEAVY METALS ON THE PHOTOPHYSICAL PROPERTIES OF PLANT LEAVES

Diego Tellería* **y** **María Gabriela Lagorio#**

* Escuela de Ciencia y tecnología, Universidad Nacional de San Martín, San Martín, Argentina, Yapeyú 2068, d_telleria@hotmail.com
\# Departamento de Química Inorgánica, Analítica y Química Física/INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina, Pabellón II Ciudad Universitaria, mgl@qi.fcen.uba.ar

Keywords: Fluorescence, reflectance, photosynthesis.

Copper is an essential micronutrient for higher plants but excess concentration of copper in the environment may induce significant toxic effects. In the present work, changes in photophysical properties of leaves exposed to copper ion were analyzed and compared to control "non-stressed" leaves. *Potus* species was used in the study.

Photophysical parameters related to photosynthesis such as the maximum quantum yield of photosystem II (F_v/F_m), the quantum yield of photosystem II (Φ_{PSII}), the proportion of open PSII (qP), and the non-photochemical quenching coefficient (qNP) were determined using a Pulse Amplitude Modulated fluorometer Hansatech FMS1. Results are reviewed in table 1.

	F_v/F_m	Φ_{PSII}	qP	qNP
Copper stressed leaves	0.40 ± 0.15	0.12 ± 0.02	0.53 ± 0.11	0.34 ± 0.10
Control leaves	0.795 ± 0.004	0.50 ± 0.02	0.85 ± 0.09	0.64 ± 0.07

Table 1. Photosynthesis parameters obtained from variable Chlorophyll-a fluorescence.

Fluorescence spectra under low photon flux were also recorded using a PTI steady-state fluorometer. Values for the fluorescence ratio at 685 and 735 nm (F_{685}/F_{735}) are shown at table 2.

	F_{685}/F_{735}
Copper stressed leaves	0.72 ± 0.11
Control leaves	0.51 ± 0.05

Table 2. Fluorescence ratio F_{685}/F_{735} obtained from initial fluorescence spectra.

The absorption and the scattering of light coefficients were determined from transmittance and reflectance values of single leaves (obtained with a spectrophotometer Shimadzu 3101 equipped with an integrating sphere) and using the Pile of Plates model. The absorption coefficient decreased in copper-stressed leaves showing a destruction of photosynthetic pigments. The scattering coefficient, on the other hand, remained almost unchanged.

It was shown that the most sensitive parameter in this work for copper toxicity was the quantum yield of PSII (Φ_{PSII}).

P112

SÍNTESIS Y CARACTERIZACIÓN DE NANOPARTICULAS FLUORESCENTES FUNCIONALIZADAS CON SAL DE PIRIDINIO

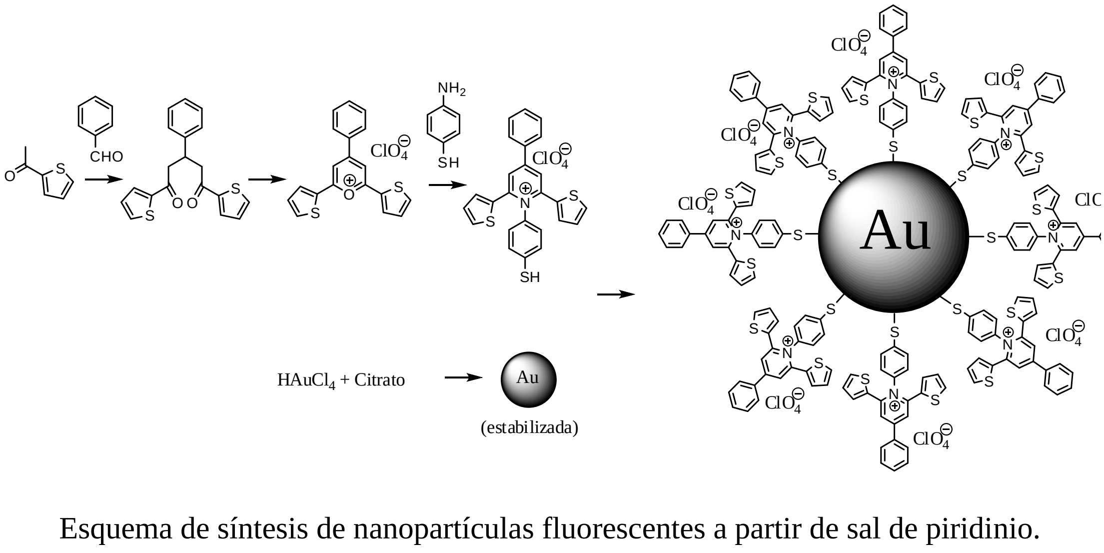
Cristian Tirapegui,[*] **Carolina Aliaga**[#]**, Marcos Caroli***

* Laboratorio de Fisicoquímica Orgánica, Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile, cristian.tirapegui@gmail.com
\# Laboratorio de Resonancia Paramagnética Electrónica, Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile,

Palabras clave: Nanopartícula de oro, fluorecscencia.

Diversas nanopartículas de oro se han preparado por distintos métodos durante los últimos años, las que han tenido aplicaciones en muchos campos de la ciencia tales como medicina, óptica, nuevos materiales, entre otros. En el presente trabajo se describe la preparación de nanopartículas a partir de la tradicional reducción de $HAuCl_4$ con citrato y el dopaje de éstas con un fluoróforo derivado de sal de piridinio, el perclorato de (1-(4-mercaptofenil)-4-fenil-2,6-di(tiofen-2-il)piridinio. El procedimiento utilizado es una proyección del clásico método de Turkevich[1] donde se reemplazó la capa estabilizante de citrato por el fluoróforo. Las nanopartículas fueron caracterizadas por light scattering y espectroscpoia UV-vis, arrojando un $\lambda_{max} \sim 550$ nm característico de la banda del plasmón para este tipo de nanopartículas[2]. Se estudió también la fotofísica de las presentes nanoparticulas y además del estudio de estabilidad en el tiempo de las mismas.

.



Esquema de síntesis de nanopartículas fluorescentes a partir de sal de piridinio.

---

1) J. Turkevich, P. C. Stevenson, J. Hillier, Discuss. Faraday. Soc. 1951, 11, 55-75;
G. Frens, Colloid & Polymer Science 1972, 250, 736-741.

2) Tao Zhu, Krasimir Vasilev, Maximilian Kreiter, Silvia Mittler, Wolfgang Knoll, *Langmuir*, Vol. 19, No. 22, 2003.

P113

ROSE BENGAL AND ERYTHROSIN B ADSORBED ON CELLULOSE: PHOTOPHYSICAL CHARACTERIZATION AND DETERMINATION OF TRIPLET QUANTUM YIELDS BY LIOAS

Eugenia Tomasini,* Enrique San Román* and Silvia E. Braslavsky*#

* INQUIMAE / DQIAyQF, Facultad de Ciencias Exactas y Naturales. Universidad de Buenos Aires, Ciudad Universitaria, Pab. II, C1428EHA Buenos Aires, Argentina, eugenia@qi.fcen.uba.ar
# Max-Plank-Institut für Bioanorganische Chemie, Postfach 101365, D 45413 Mülheim an der Ruhr, Germany

Keywords: triplet quantum yield, light scattering solid, optoacoustic spectroscopy

At present no general method exists for the determination of triplet quantum yields (Φ_{T}) for dye-loaded opaque solids. Laser induced optoacoustic spectroscopy (LIOAS), which has been successfully applied to the determination of fluorescence quantum yields of light-scattering solid samples,[1] is used in this work for the measurement of Φ_{T} for Rose Bengal (RB) and Erythrosin B (EB) adsorbed on cellulose microparticles.

Under specific conditions, the following equation, similar to that found in solution, applies:

$$\frac{(H/E)_{\mathrm{S}}}{(H/E)_{\mathrm{R}}} = \frac{(1-R)_{\mathrm{S}}}{(1-R)_{\mathrm{R}}} \left(1 - \Phi_{\mathrm{obs}} \frac{< \nu_{\mathrm{F}} >}{\nu_0} - \Phi_{\mathrm{T}} \frac{E_{\mathrm{T}}}{h\nu_0} \right)$$

where H is the first maximum of the optoacoustic signal, E is the laser pulse energy, R is the sample total reflectance, Φ_{obs} is the observed fluorescence quantum yield (affected by reabsorption), ν_0 is the laser frequency, $<\nu_{\mathrm{F}}>$ is the average fluorescence frequency, E_{T} is the triplet energy and h is the Planck constant; S and R stand for sample and reference, respectively. Brilliant Blue is used as the calorimetric reference.

Φ_{T} values around 0.54 and 0.50 are obtained for RB and EB, respectively, substantially lower than in solution (0.7 – 0.8 for RB and 0.9 – 1.0 for EB in different solvents). These values do not depend on dye loading in spite of the aggregation of both dyes on cellulose.

Observed fluorescence quantum yields of both dyes decrease with concentration by fluorescence reabsorption and dimerization. At least for RB, weak exciton coupling yields fluorescing quasi H dimers.[2]

Decreasing the polarity of the medium the S-T energy gap of xanthene dyes increases,[3] thus lowering the intersystem crossing rate. This explains the low Φ_{T} values found on cellulose. Moreover, the small exciton splitting and the wide S-T energy gap cause both exciton levels to lie above the triplet level, enhancing intersystem crossing. This compensation mechanism leads to a triplet quantum yield nearly independent of the concentration of the dye.

---

[1] E. Tomasini, E. San Román, S. E. Braslavsky, S. *Langmuir*, 25 (**2009**) 5861.

[2] H. B. Rodríguez, M.G. Lagorio, E. San Román, *Photochem. Photobiol. Sci.*, 3 (**2004**) 674.

[3] G. R. Fleming, A. W. E. Knight, J. M. Morris, R. J. S. Morrison, G. W. Robinson, *J. Am. Chem. Soc.*, 99 (**1977**) 4306.

P114

QUANTUM YIELD DETERMINATIONS IN $S_{RN}1$ TYPE REACTIONS. PHOTOINDUCED NUCLEOPHILIC SUBSTITUTION OF AROMATIC AMINES.

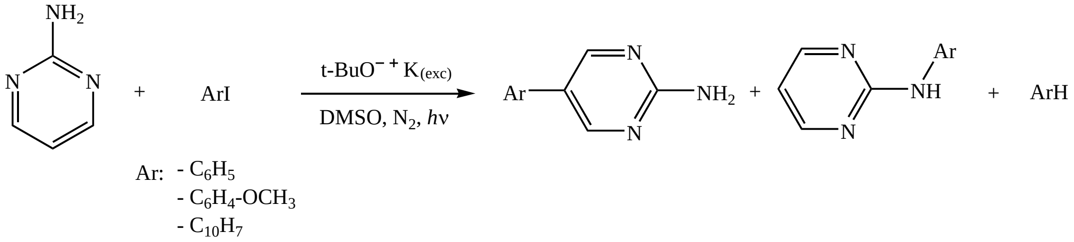
Natalia Torres, Liliana Jimenez and Adriana Pierini

INFIQC-Departamento de Qca. Orgánica, Fac. de Cs. Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina. Haya de la Torre esq. Medina Allende, Ciudad Universitaria, X5000HUA. E-mail: ljimenez@fcq.unc.edu.ar

Electron Transfer, Quantum Yield, Aromatic Amines.

Nucleophilic substitution reactions by electron transfer (**eT**) have been a powerful synthetic tool to obtain new organic compounds from substrates and nucleophiles that do not react or react slowly through S_N2 or S_N1 mechanisms. This type of reactions ($S_{RN}1$) involves electron transfer steps, generating a chain process, with radicals and radical anions as intermediates. A widely used method to initiate them is by photoestimulation.[1] Information about global quantum yields in these photoinduced **eT** reactions, which include initiation and propagation steps, provides us a better understanding of the system efficiency, involving in this context different nucleophile and substrate chemical features.[2]

Our work is based in the measurement and comparison of quantum yield values for the $S_{RN}1$ mechanism involved in the reaction of an aromatic amine set, as nucleophiles, with haloaromatic substrates. Scheme 1 represents a general reaction where 2-pyrimidinamine is one of the nucleophiles employed. It was used a benzophenone/benzhydrol system as actinometer, which permits long irradiation times (30 min *ca.*).



Scheme 1

Results show that the anions of 2-pyrimidinamine and 2,6-diethylaniline are poor electron donors leading itself to a low quantum yield for the initiation step which can be increased adding more equivalents of the base t-BuOK. The propagation quantum yields are moderate with all studied substrates, resulting in short chain lengths, around 7-8. The anion of 2-naphthalenamine presents a better initiation and also a higher propagation cycle.

References:
1 - Rossi, R.; Pierini, A.; Santiago, A. *Organic Reactions*; Paquette, L. A.; Bittman, R. Eds. Wiley, NY, **1999**.
2 - Rossi, R.; Pierini, A.; Peñeñory, A. *Chemical Reviews* **2003**, *103*, 71. Argüello, J.;

P115

ANIONIC CHEMODOSIMETERS BASED ON FLUORESCENT PYRYLIUM SALTS IN ORGANIC AND AQUEOUS SOLUTION

Eliane Torri, Vanderléia G. Marini, and Vanderlei G. Machado*

* Departamento de Química, Universidade Regional de Blumenau, FURB, Blumenau, SC, 89012–900. e–mail: gageiro@furb.br

Keywords: fluorogenic chemosensors; anion sensing; cyanide

Of the studies in the field of anion sensing, one approach studied in the recent years involves the use of chemodosimeters, which are based on processes induced by specific analytes coupled with changes in the optical properties of the system [1]. In this investigation, two pyrylium salts, **1** and **2**, were studied in acetonitrile and acetonitrile–water mixtures in the presence of various anions as tetra–*n*–butylammonium salts. These pyrylium salts are highly fluorescent chemical species in solution and it can be expected that nucleophilic anions, such as F^- and CN^-, are capable to open the pyrylium ring and yield a non–fluorescent product (**Figure 1**).

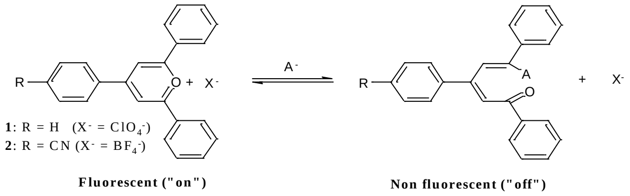


Figure 1. A chemodosimeter for anionic species based on a pyrylium salt.

In acetonitrile, OH^-, F^-, CN^-, AcO^-, and $H_2PO_4^-$ caused the quenching of the fluorescence of the compounds (**Figure 2**). However, for **1** in water or in acetonitrile–water for **2**, of the anions investigated only CN^- (and OH^-) caused the quenching in the fluorescence. Thus, addition of water to acetonitrile solutions of F^-, $H_2PO_4^-$, and CH_3COO^- salts leads to a strong preferential solvation of the anion by water, which makes the hydrated species less able to act as a base. Since CN^- is less hydrated with the addition of water, this anion is more 'naked' and therefore acts more readily as a base, promoting the abstraction of the proton from the protonated dye. Titrations of **1** and **2** with CN^- using fluorescence technique were made and showed a 1:1 chemosensor:anion stoichiometry (Figure 2C). [FURB, SED–SC, FAPESC, CNPq, INCT–Catálise].

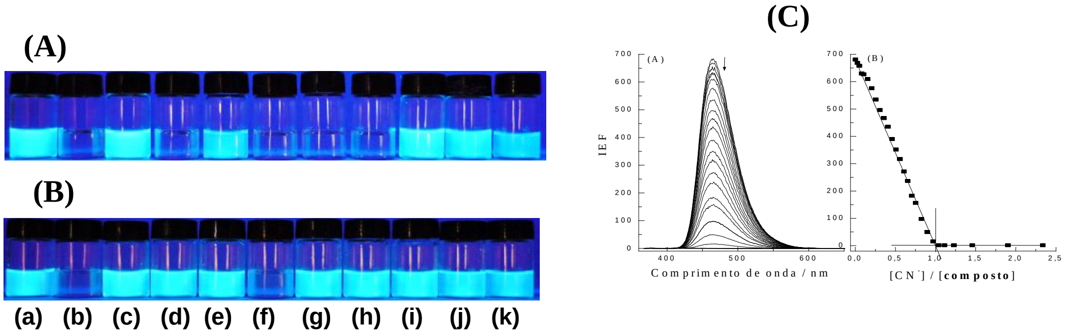


Figure 2. (A) (a) Solution of **1** in acetonitrile; (b) **1** with OH^-; **1** in presence of: (c) HSO_4^-; (d) $H_2PO_4^-$; (e) NO_3^-; (f) CN^-, (g) AcO^-; (h) F^-; (i) Cl^-; (j) Br^-, and (k) I^-. **(B)** in aqueous medium. **(C)** Emission spectra for the titration of **1** in acetonitrile with CN^- and mole ratio plot for the emission intensity of **1** at 464 nm.

[1] Martínez–Máñez, R.; Sancenón, F. *Coord. Chem. Rev.* **2006**, *250*, 3081.

P116

REACTIVIDAD DE ACETAZOLAMIDA FRENTE AL OXÍGENO MOLECULAR SINGULETE

Cristina Valencia* **Diana Patricia Henao*** **Carolina Castaño***, **Eduard Tobón***, **Antonio Zanocco**◆, **Else Lemp**◆

* 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
◆ 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

Palabras clave: Acetazolamida, oxígeno molecular singulete, fototoxicidad

La acetazolamida (5-acetamida-1,3,4-Tiadiazol-2-sulfonamida, CAS 59-66-5) es un medicamento del grupo de las sulfas que presenta entre sus propiedades farmacológicas efecto diurético y es ampliamente utilizado en el tratamiento del glaucoma. Su acción en el organismo se basa en la capacidad de inhibir la anhidrasa carbónica, enzima encargada de mantener el equilibrio iónico. Debido a la alta incidencia de estas patologías a nivel Latinoamericano, el medicamento es de uso masivo, haciendo incluso parte de los medicamentos suministrados por los servicios de salud obligatorio (POS en Colombia, ISAPRES y FONASA en Chile, y Programa Medico Obligatorio en Argentina)

Asociado al uso de este medicamento se han reportado algunos efectos secundarios adversos en tejidos expuestos a la luz como ojos y piel, por lo que resulta muy interesante estudiar su carácter fototóxico y/o fotosensibilizador evaluando la generación de especies activas del oxígeno y su reactividad, en particular considerando la participación del oxígeno molecular singulete en reacciones Tipo II, debido a que la acetazolamida fotosensibiliza la oxidación del 2,5-dimetilfurano, un eficiente apagador del oxígeno excitado.

Estudios del efecto del solvente, específicamente a través del análisis LSER permiten profundizar en el mecanismo de la fotosensibilización de la acetazolamida, privilegiando la interacción del oxígeno excitado con el segmento aromático del anillo tiodiazol, para los que se observan constantes de reactividad total del orden de 10^5 $M^{-1}s^{-1}$, medidas tanto en experimentos en estado estacionario como resueltos en el tiempo.

Agradecimientos

Los autores agradecen a la Universidad Nacional de Colombia-Sede Medellín por los aportes que permitieron la realización del presente trabajo, Dirección de Laboratorios y Dirección de Investigaciones DIME 90202018 QUIPU 20101007746.

P117

SÍNTESIS Y CARACTERIZACIÓN DEL COMPLEJO DE RUTENIO CON EL LIGANDO 6-METOXIQUINOLINA. CARÁCTER FOTOSENSIBILIZADOR DE $^1O_2(^1\Delta_g)$.

Cristina Valencia[*], Donaldo Mercado* , Juan Carlos Muñoz[♦],
Antonio Zanocco[•], Else Lemp[•]

* 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, dfmercad@unal.edu.co
[♦] Instituto de Química, Facultad de Ciencias, Universidad de Antioquia, Medellín-Colombia, Calle 67 Número 53 - 108, jcmunozac@quimica.udea.edu.co
[•] Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago-Chile, S. Livingstone 1007, Casilla 233, azanocco@ciq.uchile.cl

Palabras clave: Ru (II) 6-metoxiquinolina, fotosensibilizador, oxígeno molecular singulete

Los compuestos quinolínicos derivados de la quinina han sido evaluados en su capacidad fotosensibilizadora debido a los efectos secundarios derivados de su uso en el tratamiento y prevención de la malaria. Estos estudios permiten determinar valores de rendimiento cuántico de oxígeno molecular singulete $O_2(^1\Delta_g)$ para el núcleo 6-metoxiquinolina cercanos a la unidad en solventes como etanol y acetonitrilo, medidos en experimentos resueltos en el tiempo y con constantes de reactividad k_r medidas en experimentos en estado estacionario del orden de 10^5 $M^{-1}s^{-}1$.

Estas características nos conducen a la síntesis del complejo de rutenio (II) con el ligando 6-metoxiquinolina, con el propósito de llevarlo a una matriz sólida, preservar su potencial fotosensibilizador y aportar al complejo estabilidad térmica y fotoquímica, que permita su futura aplicación en fotocatálisis, específicamente en procesos de desinfección de aguas y/o tratamiento de contaminantes orgánicos. Se realiza entonces la de síntesis convencional llevando a reflujo por un período de 48 horas el óxido de rutenio (II) con adiciones del ligando 6-metoxiquinolina en atmósfera inerte (N_2). Luego de generado el complejo se filtra a temperatura ambiente y recristaliza para su caracterización morfológica por medio de microscopia óptica y análisis de estabilidad térmica por medio de análisis termogravimétricos (TGA). Se evalúa su potencial fotosensibilizador en la generación de $^1O_2$ $(^1\Delta_g)$ por actinometría en condiciones de radiación en estado estacionario.

Agradecimientos

Los autores agradecen a la Universidad Nacional de Colombia-Sede Medellín por los aportes que permitieron la realización del presente trabajo, Dirección de Laboratorios y Dirección de Investigaciones DIME 90202039, QUIPU 20101008123.

P118

FOTOOXIDACIÓN DE QUINOLONAS FLUORADAS DE APLICACIÓN OFTALMOLÓGICA TÓPICA

Fabiana Vaquero y Susana Criado

Departamento de Química, Fac. de Ciencias Exactas, Fisicoquímicas y Naturales, Universidad Nacional de Río Cuarto. Enlace rutas 8 y 36. Km 603. Río Cuarto (Córdoba). Argentina. e-mail: scriado@exa.unrc.edu.ar

Palabras clave: quinolonas fluoradas, fotodegradación, especies reactivas de oxígeno

Las fotorreacciones promovidas por luz medioambiental de moléculas de importancia oftalmológica han despertado un especial interés en las últimas décadas debido a que dichas reacciones pueden producir no solamente la disminución de la eficacia terapéutica de los principios activos de los fármacos sino también generar compuestos nocivos por su toxicidad. Aunque la mayoría de estos principios activos son transparentes a la radiación lumínica natural, la fotodegradación puede ser promovida por pigmentos presentes en el órgano ocular. En particular Riboflavina (componente del complejo vitamínico B_2) es un sensibilizador natural capaz de absorber dicha radiación y producir especies electrónicamente excitadas, las cuales pueden inducir, de forma directa o indirecta, procesos fotoquímicos sobre los principios activos de fármacos oftálmicos de uso tópico.

Aquí presentamos resultados acerca de la cinética y mecanismos de fotooxidación sensibilizada de las quinolonas fluoradas (QF): Ácido Nalidixico, Ciprofloxacina, Lomefloxacina y Norfloxacina, las cuales son utilizadas como agentes antimicrobianos de aplicación oftálmica tópica.

Los resultados indican que las QF, en concentraciones milimolares, interactúan con el estado triplete electrónicamente excitado de Riboflavina, como así también con las especies reactivas de oxígeno (ROS) generadas a partir de dicho estado. La participación de las diferentes ROS (oxígeno singlete, radical hidroxilo, anión radical superóxido y peróxido de hidrógeno) en el proceso de fotodegradación sensibilizada de QF fue determinada a través del uso de inhibidores específicos de tales especies oxidantes. La discusión se realiza en base al peso relativo de cada especie en el mecanismo de degradación de las QF bajo diferentes condiciones experimentales.

P119

SENSIBILIDAD FOTOQUÍMICA DE CÉLULAS EPITELIALES DE CRISTALINO DE BOVINO (BLEC) EXPUESTAS A RADIACIÓN UVA-VISIBLE EN PRESENCIA DE PRODUCTOS DE GLICACIÓN AVANZADOS Y DE OTROS SENSIBILIZADORES ENDÓGENOS. SU EFECTO EN SISTEMAS PROTECTORES

Francisco Vargas[1], María I. Becker [2], Bertrand Friguet [3] & Eduardo Silva[1].

[1]Facultad de Química, Pontificia Universidad Católica de Chile, Laboratorio de Química Biológica. E-mail:fvargasn@uc.cl:.[2] Laboratorio de Investigación y Desarrollo, Biosonda.

[3] Laboratoire de Biologie et Biochimie Cellulaire du Vieillissement. UR4 Vieillissement, Stress et Inflammation. Université Pierre et Marie Curie - Paris 6

Palabras claves: Sensibilidad fotoquímica, Cataractogénesis, Proteasoma.

La formación de productos de glicación avanzada (AGEs) por medio de la reacción de Maillard, es uno de los principales mecanismos involucrados en la cataratogénesis. El lente ocular está permanentemente expuesto a la luz, y la presencia de sensibilizadores endógenos como los AGEs permite que ocurran fenómenos fotoquímicos que generan estrés oxidativo.

Estudios previos han mostrado la potencial actividad fotosensibilizante de AGEs derivados de ascórbico, utilizando como modelos la fotodescomposición del aminoácido triptófano y la inactivación de la enzima glucosa-6-fosfato deshidrogenasa. En el presente trabajo se estudió el efecto de los productos de glicación avanzada derivados de glucosa y ascorbato y otros sensibilizadores endógenos sobre células epiteliales de lente de bovino expuestas a luz UVA-Visible y el efecto que estos producen en los sistemas protectores celulares, como lo son las enzimas glucosa 6 fosfato deshidrogenada, glutatión reductasa y el proteasoma.

AGRADECIMIENTOS

Los autores agradecen el financiamiento otorgado por el proyecto FONDECYT 1050965. Francisco Vargas agradece financiamiento de Beca Doctoral Proyecto MECESUP.Francisco Vargas agradece financiamiento de Estadía Doctoral por Becas Chile 2009.

P120

OPTICAL PROPERTIES OF ZIRCONIUM (IV) AND HAFNIUM (IV) TETRA-PHENIL PORPHYRIN COMPLEXES

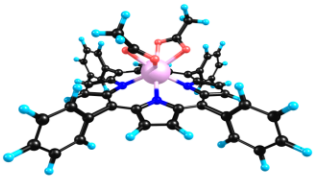
Ricardo Veloso B.[*] **, Alvaro Muñoz-Castro*, Ramiro Arratia-Perez* and Luis Alvarez-Thon**[$]

* Departamento de Ciencias Químicas, Facultad de Ecologia y Recursos Naturales, Universidad Andres Bello, Santiago, Chile, Republica 275, ric24500@gmail.com
$ Departamento de Física, Facultad de Ingeniería, Universidad Andrés Bello, Santiago, Chile, Republica 275.

Palabras clave: TPP, Heavy Metal, DFT.

The optical properties of organic compounds can be considerably modified by the coordination to metal ions. In this field, porphyrin complexes constitute an important family of luminescent coordination compounds (1). These features are of great interest due to their applications as sensors, biological probes and electronic devices, among others (1). In this study, two complexes bis(acetato)hafnium(IV) and bis(acetato)zirconium(IV) of 5, 10, 15, 20-tetraphenilporphyrin were modeled by Relativistic DFT methods. Both complexes show fluorescence, a common phenomenon in porphyrin complexes but the Hf complex show furthermore a coexisting phosphorescence (1, 2).

Our objective is to explain and understand this behavior and the relationship between the relativistic effects and luminescent properties of these complexes.



Two complexes was studied here, bis(acetato)hafnium(IV) and bis(acetato)zirconium(IV) of TPP

All calculations were made with the Amsterdam Density Functional code (ADF2008.01 and ADF2009.01). Geometry and Fragment calculations were done via the PW91 functional using TZ2P basis. Relativistic effects were taking into account via the two-component ZORA Hamiltonian. TDDFT singlet and triplet calculations were done at the optimized geometries, using the SAOP functional and the TZ2P basis.

We have observed that relativistic effects induce great changes in orbital energies and their spin distribution, this is true, especially in the case of Hf complex and where the shielding of s and p atomic orbital influences a destabilization of the d orbital energy levels with respect to nonrelativistic results (indirect relativistic effect). Thus, it is possible to assign and explain their UV absorption spectra which are assigned here to be intraligand charge transfer bands (ILCT).

Bibliography

1. Knor, G., Strasse, A., Inorg. Chem. Comm., 5, 993(2002).
2. Knor, G., Strasse, A., Inorg. Chem. Comm., 8, 5, 471(2005)

Acknowledgments: The author thanks the financial support of FONDECYT 1070345; Beca Doctoral FQM-UNAB, DI-09-09/I, DI-09-06/I, DI-02-09/R, Millenium Nucleus P07-006-F.

P121

Production of superoxide anion by aromatic pterins under UV radiation

Mariana Vignoni,* **M. Laura Dántola,* Carolina Lorente,* Patricia Vicendo,[#] Esther Oliveros[#] 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: athomas@inifta.unlp.edu.ar

Laboratoire des IMRCP, UMR CNRS 5623, Université de Toulouse (Paul Sabatier), 118, route de Narbonne, F-31062 Toulouse cédex 9, France.

Palabras clave: pterins, superoxide anion, UV-A

Pterins, heterocyclic compounds widespread in living systems, participate in relevant biological processes, such as metabolic redox reactions.(1) Under UV-A excitation (320–400 nm), pterins can fluoresce, undergo photooxidation to produce different products, generate reactive oxygen species (ROS)(2) and photoinduce oxidation of biomolecules through electron transfer mechanisms. In this work, we investigated electron transfer pathways initiated by excited states of pterins generated by UV-A radiation.

The generation of superoxide anion ($O_2^{\bullet-}$) was investigated by electron paramagnetic resonance (EPR), using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as spin-trap.(3) To confirm the formation of $O_2^{\bullet-}$ upon pterin (Ptr) photolysis, EPR experiments were performed in the presence of superoxide dismutase (SOD), enzyme that catalyzes the conversion of $O_2^{\bullet-}$ into H_2O_2 and O_2. In addition, photolysis of Ptr in the presence and in the absence of SOD was carried out. Irradiated solutions were analyzed by UV/VIS spectrophotometry, HPLC and an enzymatic method for H_2O_2 determination.

The obtained EPR spectra correspond to the adduct DMPO-OOH, which suggest that DMPO has trapped superoxide anion. Moreover, the addition of SOD caused a drastic decrease of the EPR signal, confirming the formation of $O_2^{\bullet-}$ in Ptr solutions upon UV-A irradiation. In another set of experiments, the rate of H_2O_2 formation in the presence of SOD was much higher than that measured in its absence. This result is in agreement with the data obtained in EPR experiments, but also implies the existence of recombination reactions that consume most $O_2^{\bullet-}$ formed in the absence of SOD. Taking into account all the results, the following mechanism can be proposed

$$\begin{aligned}
\text{Ptr}^* + \text{Ptr} &\longrightarrow \text{Ptr}^{\bullet+} + \text{Ptr}^{\bullet-}\\
\text{Ptr}^{\bullet-} + O_2 &\longrightarrow \text{Ptr} + O_2^{\bullet-}\\
2H^+ + O_2^{\bullet-} &\longrightarrow H_2O_2 + O_2\\
\text{Ptr}^{\bullet+} + O_2^{\bullet-} &\longrightarrow \text{Ptr} + O_2
\end{aligned}$$

References

(1) W. Pfleiderer, in *Chemistry and Biology of Pteridines and Folates,* Plenum Press, New York, 1993, pp. 1-16

(2) C. Lorente, A. H. Thomas, *Acc. Chem. Res.*2006, 39, 395-402

(3) E. Finkelstein, G. M. Rosen and E. J., *Arch. Biochem. Biophys.* 1980, 200, 1-16

P122

UN ESTUDIO CINÉTICO DE LA REACCIÓN DE RADICALES SULFATO Y DIHIDRÓGENO FOSFATO CON EPICATEQUINA, EPICATEQUINGALATO Y EPIGALOCATEQUINGALATO

Laura S. Villata*, Mónica C. Gonzalez#, y Daniel O. Mártire♦

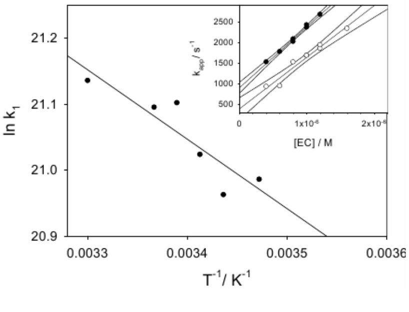
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata. La Plata, Argentina.
* laura@inifta.unlp.edu.ar, # gonzalez@inifta.unlp.edu.ar, ♦ dmartire@inifta.unlp.edu.ar

Los flavonoides son sustancias polifenólicas que presentan conocida acción antioxidante y que forman parte de una gran cantidad de productos naturales. Se han realizado estudios cinéticos a partir de algunos flavonoides: epicatequina (EC), epicatequingalato (ECG) y epigalocatequingalato (EGCG) con radicales fuertemente oxidantes generados fotoquímicamente. A partir de las constantes de decaimiento aparente (k_{app}) de los radicales en presencia de concentraciones variables de flavonoides se obtuvieron las constantes bimoleculares para la reacción entre los polifenoles y los radicales. En la siguiente tabla se presentan estas constantes de velocidad para las reacciones con radical sulfato y dihidrógeno fosfato.

Flavonoide(Ar-OH)	k (X + Ar-OH), $M^{-1}s^{-1}$	
	$SO_4^{\cdot-}$	H_2PO_4
EC	$(1.46\pm 0.06) \times 10^9$	$(7.8\pm 0.9) \times 10^8$
ECG	$(1.20 \pm 0.08) \times 10^9$	$(8.5\pm 0.4) \times 10^8$
EGCG	$(1.04 \pm 0.07) \times 10^9$	$(6.8\pm 0.4) \times 10^8$

Se ha estudiado el efecto de la temperatura sobre la reacción de EC y $SO_4^{\cdot-}$. La energía de activación [E_A = (9 ± 3) $kJmol^{-1}$] y el factor prexponencial [$A = (4.8 \pm 0.6) \times 10^{10}$] fueron evaluados en el intervalo de temperatura 288- 303 K.

En la figura se puede observar esta dependencia y la variación de k_{app} con [EC] a 295 K (●), y 291 K (○)



A partir de datos obtenidos en nuestro laboratorio y bibliográficos se ha realizado una correlación entre las constantes de velocidad y la variación de energía libre de la reacción de transferencia de carga entre distintos antioxidantes y una serie de radicales, a fin de predecir constantes de velocidad para procesos que involucren este tipo de sustancias.

P123

LIGHT-SENSITIVE CHROMONES FOR RECORDING MEDIA OF ARCHIVAL 3D OPTICAL MEMORY

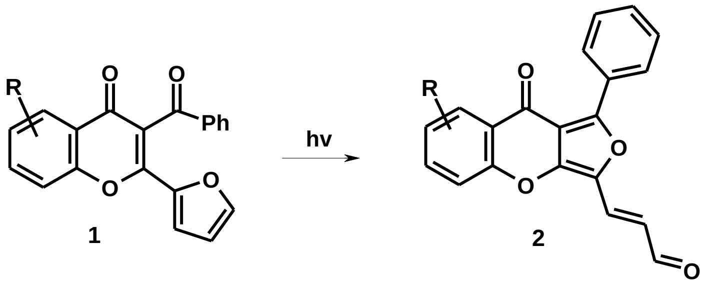
Vladimir N. Yarovenko[a], **Mikhail M. Krayushkin**[a], **Konstantin S. Levchenko**[a], **Ol'ga I. Kobeleva**[b], **Tat'yana M. Valova**[b], **Valery A. Barachevsky**[b]

[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991, Moscow, Russia. E-mail: yarov@ioc.ac.ru .

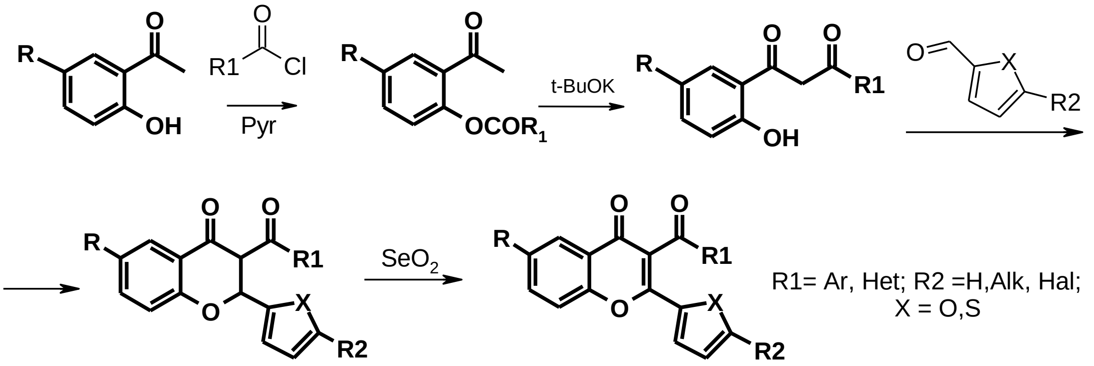
[b]Institution of the Russian Academy of Sciences, Photochemistry Center of RAS, Moscow, Russia, 119421, 7a-1, Novatorov Str., barva@photonics.ru

Compounds undergoing irreversible changes under ultraviolet irradiation with formation of photoluminescent products, which provide optical information read-out, are of considerable interest for the development of novel recording media for multilayer bitwise archival three-dimensional optical memory.

We showed that it is reasonable to use chromone derivatives (1) as above substances. Compounds 1 are not fluorophores themselves but under irradiation undergo irreversible transformation into the fluorescing products 2.



The synthetic methods were developed and the photochemical properties were studied for a wide range of earlier unknown analogues of chromone derivatives 1 and fluorescent products of their transformation 2.



R1= Ar, Het; R2 =H,Alk, Hal;
X = O,S

P124

ESTUDIO DE LA REACCIÓN QUÍMICA ENTRE QUERCITINA Y OXÍGENO MOLECULAR SINGULETE EN MEZCLA METANOL-AGUA

Antonio L. Zanocco, Alejandro Soto, Pablo Fuentes, Catalina Sandoval, Javier Morales, Germán Günther y Else Lemp

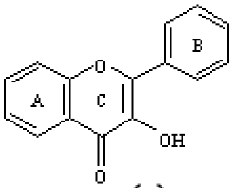
Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Fisicoquímica, Casilla 233, Santiago - 1, Santiago, Chile. e-mail: elemp@ciq.uchile.cl

Palabras Clave: flavonoides, oxígeno molecular singulete, efecto solvente.

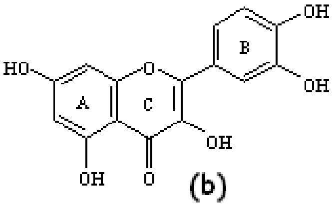
Los flavonoides son una familia de compuestos que se biosintetizan en todas las plantas, cumplen en ellas diferentes funciones metabólicas y son responsables de protegerlas de la fotooxidación debida a luz UV proveniente del sol. El hombre, al consumir vegetales, incorpora estas especies a su organismo. Se ha demostrado que los flavonoides en el organismo humano exhiben propiedades como antimicrobianos y anticancerígenos.

El oxígeno molecular singulete, O_2 ($^1\Delta_g$), es una de las denominadas especies reactivas del oxígeno. Su generación en el organismo humano es un proceso normal, así como la presencia de especies químicas capaces de desactivarlo. Existen diversas especies que desactivan al O_2 ($^1\Delta_g$), entre ellas los flavonoides, conocidos antioxidantes, que ayudarán a controlar los desbalances en la generación del oxígeno excitado en el medio biológico.

Este estudio se realiza para determinar las diferencias de reactividad para las reacciones entre O_2 ($^1\Delta_g$) y dos flavonoides de diferente estructura, 3-hidroxiflavona (a) y con quercitina (b) en mezclas metanol-agua. Para la quercitina se espera que el oxígeno excitado interaccione con más de un sitio reactivo, a diferencia del mecanismo corrientemente aceptado, que involucra el ataque electrofílico del oxígeno excitado a la posición 3 del anillo C del flavonoide.



(a)



(b)

Los resultados encontrados muestran comportamientos significativamente diferentes en la reactividad de los flavonoides (a) y (b) en mezclas metanol agua de diferente composición.

Se agradece el financiamiento de Proyecto Fondecyt Nº 1090267

P125

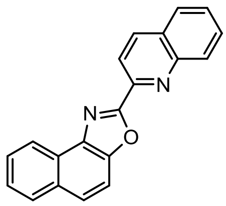
SOLVENT EFFECT ON THE PHOTOPHYSICS OF BENZOTHIAZOLE AND NAPHTHOXAZOLE QUINOLIN DERIVATIVES

Renzo P. Zanocco,[1] Silvana Valdebenito,[1] Yasser Gidi,[1]Antonio L. Zanocco[1],
Xavier Ragàs,[2] Santi Nonell.[2]

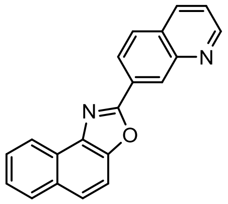
[1]Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Fisicoquímica, Casilla 233, Santiago - 1, Santiago, Chile. e-mail: azanocco@ciq.uchile.cl
[2]Grup d'Enginyeria Molecular, Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, E-08017, Barcelona, España

Keywords: Fluorescence, Naphthoxazole, Solvent Effect

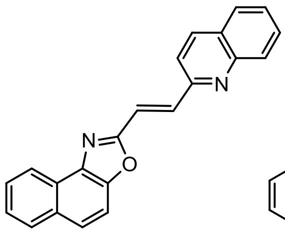
The highly favorable photophysical properties of benzoxazole and benzothiazole derivatives, such as high fluorescence quantum yield, photostability, as well as the easy tuning of their photophysical properties by changing a substituent at position 2 in the heterocyclic ring, endow these compounds with high potential as new fluorophores. Derivatives of these compounds have been used in industrial, biological and analytical applications. They are also efficient probes for monitoring and exploring the properties of micelles, the hydrophobic interactions in human serum albumin, and employed in a promising and convenient fluorescent molecular sensing strategy based on a dual "lock–key" mechanism. In spite of the wide range of basic and innovative research, to the best of our knowledge no reports exist on the photophysic and/or the photochemistry of compounds with the heterocyclic ring condensed to extended aromatic systems, or including aromatic heterocyclic substituents in position 2. Building on the fact that the benzoxazole and benzothiazole excited states have substantial charge-transfer character, we hypothesized that naphtho- for benzo-ring change and/or including heteroaromatic substituents in position 2, could substantially affect the photophysical properties of these compounds. In this work we report the results of the study of solvent effect on the absorptive and emissive characteristics of compounds in the figure:



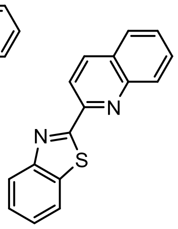
2-(quinolin-2-yl)naphtho
[1,2-*d*]oxazole



2-(quinolin-7-yl)naphtho
[1,2-*d*]oxazole



(*E*)-2-(2-(quinolin-2-yl)vinyl)naphtho
[1,2-*d*]oxazole



2-(quinolin-2-yl)benzo
[*d*]thiazole

Results obtained employing steady state and time resolved techniques shows that oxazole derivatives have fluorescence quantum yields ranging between 0.5 – 1, fluorescence lifetime in the order of 1 – 3 ns and fluorescence spectra largely dependent on the solvent polarity. Replacement of oxygen by sulfur atom dramatically decreases the fluorescence quantum yield and the Stokes shift, indicating that the oxygen atom in the heterocyclic ring plays a critical role determining the photophysical properties, making these compounds valuable candidates for technological applications as dyes, sensitizers, quantum counters, or fluorescent probes.

Acknowledgements
Financial support from FONDECYT (grant 1080410) is gratefully acknowledged

LASER FLASH PHOTOLYSIS STUDY OF THE PHOTOCHEMISTRY OF THIOXANTHONE IN LAPONITE CLAY.

Lisbeth Zelayaran Melgar[*], **Miguel G. Neumann, Carla C. S. Cavalheiro**

Universidade de São Paulo, Instituto de Química de São Carlos, Departamento de Físico-Química, Avenida Trabalhador São-Carlense, 400 São Carlos, SP, lisbethzm@gmail.com

Key Words: thioxanthone (TX), triplet-triplet absorption, clay

In solid state, photochemical methods have been applied to the study of several organic compounds adsorbed or included in many solid powdered substrates such as silicalite, silicas, cyclodextrins and clays[1]. Notwithstanding, photophysical and photochemical studies involving TX on clays are not available in the literature. Laponite consists of very fine clay particles with an average diameter of 10 nm. The surface of a dried laponite particle is built up of an outer surface that involves siloxane bonds and a lateral surface of the layers that include broken and terminated Si-O and Mg-O and/or Li-O bonds. The particle also includes an interlayer surface partially covered by Na^+ cations.

Thioxanthone are efficiently and extensively used as photoinitiators in dentistry resins and photopolymerization systems[2].

Transient absorption spectra and triplet decay curves of the degassed TX/clay solid matrices were measured at room temperature using the laser flash photolysis technique.

Transient absorption spectra recorded 1.6 μs after laser excitation at 355 nm of TX adsorption on Laponite (0.5% percentage mass) in state solid shows a shoulder at 470 nm and two maxima at 605 and 740 nm. The 605 nm peak and shoulder at 470 nm have already been identified as corresponding to the TX triplet and ketyl radical, respectively[2]. We assign the 740 nm peaks to the TX radical anion. The optical spectra of TX and Xanthone radical anion has been previously reported to have a broad absorbance at 650 and 610 nm, respectively[3]. The λ_{max} for triplet-triplet absorption shows the bathochromic shift with increasing of the TX concentration on the clay (0.5, 1 and 1.5% percentage mass of TX/clay). The triplet-triplet absorption maxima is similar to these determined for TX transient absorption in polar/hydroxylic solvents.

The decay curves of the transient absorption of TX (observed at 605 nm) exhibit three components. The ^{3}TX lifetimes on laponite clay are 6.12, 25.31 and 110.90 μs with 0.5% percentage mass of TX/clay. The triplets are longer lived on the laponite clay surface than in homogeneous solution. When increasing the TX concentration on the clay, the ^{3}TX lifetime is reduced due to self-quenching.

Acknowledgment: L.Z.M. Thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for a postdoctoral fellowship and FAPESP.

1. F. Wilkinson, G.P. Kelly, in: M. Anpo, T. Matsuara (Eds.), Photochemistry on Solid Surfaces, Elsevier, Amsterdam, 1989, 31.
2.Ferreira G. C.; Carla C. Schmitt; Neumann M. G.; J. Braz. Chem. Soc., 2006, 17, 5, 905.
3.Yates, S. F.; Schuster, G. B.; J. Org. Chem., 1984,49,3349.

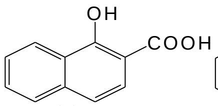
P127

PHOTOCHEMISTRY OF NAPHTHALENE DERIVATIVES IN THE PRESENCE OF GOLD (III) IN AQUEOUS MEDIUM

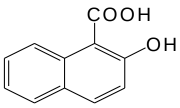
Lizandra M. Zimmermann*, **Haidi D. Fiedler e Faruk Nome#**
* lizazimer@yahoo.com.br
# Department of Chemistry, Federal University of Santa Catarina / National Institute – INCT-Catálise, Campus Trindade CEP: 88040-900
Florianópolis – Santa Catarina – Brazil.

Keywords: Gold (III), organometallic complexation, fluorescence

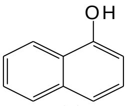
Since metal ions strongly affect the photochemistry of organic probes,[1] the photochemical properties of fluorescent compounds (see **1-6**) in aqueous medium (pH=5,0, buffer acid / acetate) was investigated as a function of [Au^{3+}]. Solutions of the probes ($1,0\times10^{-5}$ mol dm^{-3}) were titrated with increasing amounts of Au^{3+} to evaluate the response of fluorescence, absorbance and lifetime on the interaction of the probe with the metal ion. Probes **1-6** were selected to analyze the importance of structural changes in the photochemical behavior in the presence of Au^{3+}.



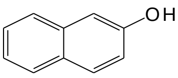
(1)



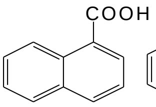
(2)



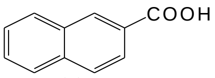
(3)



(4)



(5)



(6)

Quantitative studies showed formation of complexes between the organic probes and Au^{3+}, and suppression of fluorescence was observed, depending on the functional groups present in the probes (Figure 1). Fluorescence quenching effect was found to the two isomers of hydroxy-naphthoic acids (**1** and **2**) with similar spectrum profile obtained to their naphthols (**3** and **4**) where OH group is in the same position. However, naphthoic acids did not show fluorescence quenching effect by Au^{3+} addition. In order to understand the dynamics of the processes, lifetimes for different systems were measured as a function of Au^{3+} and the data treated with complexation models.

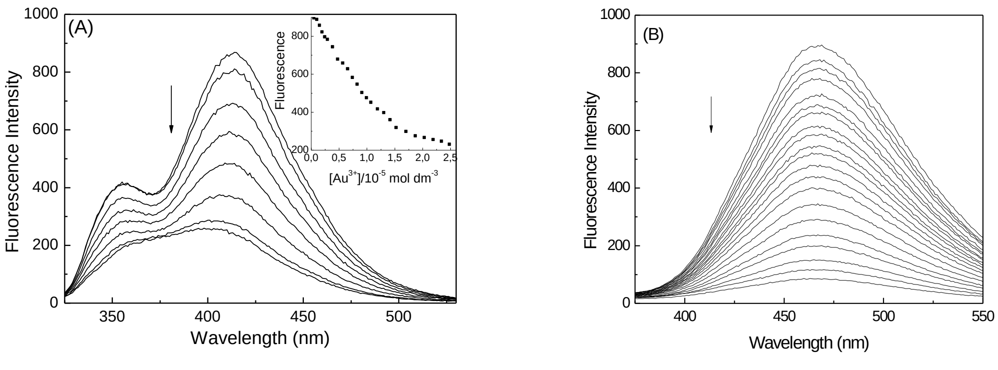


Figure 1. (*A*) Emission spectra of compound **2** with excitation at 280 nm as function of [Au^{3+}] up to 2.5×10^{-5} mol dm^{-3}. **Insert**: emission intensity of **2** at 415 nm versus [Au^{3+}]. (*B*) Emission spectra of compound **3** with excitation at 290 nm as function of [Au^{3+}] up to 2.5×10^{-5} mol dm^{-3}.

References

1. L.V. Vargas, J. Sand, T.A.S. Brandão, H.D. Fiedler, F.H. Quina, F. Nome, Analyst 130 (2005) 242.

TITLE INDEX

PLENARY CONFERENCES

ORAL PRESENTATIONS

POSTERS PRESENTATIONS

AUTHOR INDEX