General information about the European

Photochemistry Association

is available at:

www.photochemistry.eu

Newsletter Editor: Dr. David WORRALL

Department of Chemistry, Loughborough University,
Leicestershire LE11 3TU, UK
Tel: +44(0)1509 222567, Fax: +44(0)1509 223925,
email : d.r.worrall@lboro.ac.uk web :
http://www.lboro.ac.uk

ISSN 1011-4246

Printed in Italy, Bononia University Press, via Farini 37, 40124
Bologna

CONTENTS

EPA EXECUTIVE COMMITTEE

Chair
Dr. Dimitra Markovitsi
Francis Perrin Laboratory,
CEA-CNRS URA 2453
CEA/Saclay
91191 Gif-sur-Yvette, France
Tel +33(0)1 6908 4644
Fax +33(0)1 6908 8707
Email: dimitra.markovitse@cea.fr
Web: http://www-lfp.cea.fr/

Vice-Chairman
Prof. Dr. Helge Lemmetyinen
Department of Materials Chemistry
Tampere University of Technology
P.O. Box 589
FIN - 33101 Tampere
Finland
Tel: +358/31/3162565
Fax: +358/31/3162108
Email: helge.lemmetyinen@tut.fi

Treasurer
Dr. Silvio Canonica
EAWAG
Ueberlandstrassse 133
CH-8600 Duebendorf
Switzerland
Tel: +41 44 823 54 53
Fax: +41 44 823 52 10
Email: canonica@eawag.ch

Membership

Prof. Dr. Nina P.Gritsan
Institute of Chemical Kinetics and
Combustion of SB RAS
630090 Novosibirsk,
Russia
Email: gritsan@ns.kinetics.nsc.ru

Public Relations

Prof. Dr. Werner NAU
School of Engineering and Science of
Chemistry
Jacobs University
Campus Ring 1
D-28759 BREMEN
Germany
Email: w.nau@jacobs-university.de

Past Chair

Prof. Dr. David Phillips
Department of Chemistry
Imperial College London
South Kensington campus
London SW7 2AZ
England
Tel: +44 (0)20 7594 5716
Fax: +44 (0)20 7594 5812
Email: d.phillips@imperial.ac.uk

Responsible for PPS matters:

Dr. Sandra Monti
Molecular Photoscience Group
Institute I.S.O.F.-C.N.R.
Area della Ricerca
Via P. Gobetti, 101
40129-Bologna (Italy)
Tel: +39/51/6399813
Fax: +39/51/6399844
Email: monti@isof.cnr.it

Newsletter Editor:

Dr. David Worrall
Photochemistry Research Group
Department of Chemistry
Loughborough University
Leicestershire LE11 3TU, UK
Tel: +44(0)1509 222567
Fax: +44(0)1509 223925
Email: d.r.worrall@lboro.ac.uk

Website manager:

Prof. Dr. Eric Vauthey
Department of Physical Chemistry
University of Geneva
30 quai Ernest-Ansermet,
CH-1211 Geneve 4
Switzerland
Tel +41(0)22 379 6537
Fax +41(0)22 379 6518
Email: eric.vauthey@chiphy.unige.ch

EDITORIAL

Chair's Letter

Dear Colleagues,

Many of you have requested a printed version of the Newsletter. Despite the practical advantages of the modern electronic edition, turning over the pages of a small booklet which is easy to transport in a pocket or in a bag still remains attractive. Therefore here it is, resulting from combined efforts in the north and the south of Europe: the document you have in your hands was prepared in the UK and printed in Italy.

One important role of the Newsletter is to present the photochemistry activities in various European countries. In the last issue, you have read an extended description of the UK groups. Here you will find news from Italy, which has a long tradition in photochemistry, but also from countries with fewer members - Austria and Greece. If you have not had the possibility of participating in national photochemical societies/groups, you are invited to make your work known amongst our community via this Newsletter. You can also exchange information and views using the discussion forum on our website (www.photochemistry.eu) and the electronic mailing list of members.

In 2006, the Executive Committee had decided to offer a Prize for the best PhD Thesis in Photochemistry. Twenty three candidates have been nominated by EPA members for the first Prize (page 11), and their work has been examined by four independent referees. The selection has not been an easy task because of the many excellent studies. Therefore, it was decided that the 2008 Prize will be split equally between two candidates. The winners are Maria Abrahamsson ("Tuning of the excited state properties of ruthenium (II) polypyridyl complexes"; University of Uppsala, Sweden) and Alexander Fürstenberg ("Ultrafast Excited-State Dynamics in Biological and in Organised Environments"; University of Geneva, Switzerland). Both will present their PhD research at the forthcoming IUPAC Symposium on Photochemistry to be held in Gothenburg, Sweden (page 151). I warmly congratulate the winners but also all of the nominees because their nomination is a special distinction in our community.

From now on you will receive an electronic alert as soon as an issue of *Photochemical & Photobiological Sciences*, the official Journal of the Association (back cover), is published. This will allow you to have a look at the contents in the issue and access papers that are of interest to you. If you have problems accessing the Journal please contact Sarah Ruthven (ruthvens@rsc.org) and she will send you your login and password details.

We are also in the process of preparing a flyer with the aim of making EPA known to a larger scientific community. This will be ready for Gothenburg where the EPA General Assembly will take place on Thursday 31st of July at 18:15. The Executive Committee will present last year's actions, new projects and will propose a revision of the statutes. Such a change is necessary in order to adapt to the evolution of scientific and institutional context in Europe.

I am looking forward to meeting you in Sweden

Dimitra Markovitsi

EPA Chair

Grammaticakis-Neumann Prize 2008

Call for Nominations

The Photochemistry Section of the Swiss Chemical Society (which acts as the Swiss section of the European Photochemistry Association, EPA) is pleased to invite nominations for the International Grammaticakis-Neumann Prize 2008.

The Prize consists of a diploma and a financial award of SFr 5'000 (for each awardee, if there is tmore than one), and it is presented once a year to a young research scientist (<40 at the time when he or she receives the prize) from academia or from industry for outstanding contributions to the science of photochemistry.

The Prize, for which nominations are now being invited, will be presented during the 2009 Fall Meeting of the Swiss Chemical Society. The award ceremony will be followed by a lecture of the laureate which is also to be published in the offical EPA journal, *Photochemical and Photobiological Sciences.*

Each member of the EPA can nominate an individual as candidate a for the Grammaticakis-Neumann Prize. Such nominations, accompanied by supporting documentation (curriculum vitae, list of publications, and supporting letters), should be submitted to the executive director of the Swiss Chemical Society by e-mail (with attachments) to Dr. Lukas Weber (info@swiss-chem-soc.ch). The closing date for nominations is October 1, 2008.

Previous laureates of the Grammaticakis-Neumann Prize are Alberto Credi (2006), Torsten Fiebig and Achim Wagenknecht (2005), Dario Bassani (2004), Johan Hofkens (2002), Nicola Armaroli (2001), Dirk Guldi (2000), Werner Nau and Eric Vauthey (1999), Axel Griesbeck (1997), Matthew Zimmt (1996). Luisa de Cola (1995), Pedro Aramendia (1994), Mark van der Auweraer (1992), V. Ramamurthy (1991), Wolfgang Rettig (1990), Martin Demuth (1987), Ian Gould and Anthony Harriman (1985). The prize is only given if worthy candidates are proposed.

NOMINATIONS FOR THE FIRST EPA PHD PRIZE

Candidate	Country	Title
ABRAHAMSSON Maria	Sweden	Tuning of the excited state properties of ruthenium (II) polypyridyl complexes
ACCORSI Gianluca	Italy	Trivalent lanthanide ions: luminescence and applications
BAGGERMAN Jacob	The Netherlands	Photoactive hydrogen-bonded rotaxanes
BERANEK Radim	Germany	From photocatalysis to optoelectronic switches: studies of visible light active photoelectrodes based on surface modified titanium dioxide
BERGAMINI Giacomo	Italy	Photo and redox active supramolecular systems
CANTAU Christophe	France	New materials for visible-light photocatalysis: from elaboration to implementation
DEROO Stéphanie	Belgium	Photochemistry of phtooxidant Ru(II) complexes in the presence of amino acids or anchored in oligonucleotidic probes and on biodegradable polymers

ENG Mathias	Sweden	Triplet excitation energy transfer in donor-bridge-acceptor systems: experimental and theoretical investigations
FERNANDES Fabio Monteiro	Portugal	Biophysical studies of membrane proteins/peptides. interaction with lipids and drugs
FRON Eduard	Belgium	Femtosecond transient absorption of donor acceptor systems
FURSTENBERG Alexandre	Switzerland	Ultrafast excited-state dynamics in biological and in organised environments
HENNIG Andreas	Germany	Development of two novel fluorescent enzyme assays: nanoTRF and supramolecular tandem assays
MENDIVE Cecilia	Argentina	Effect of UVA light on chemical reactions at the interface metal oxide/aqueous solution
MORANT MINANA Maria Carmen	Spain	Regio- and stereo-differentiation in processes photosynthesised by aromatic compounds
NORONHA Melinda Carmen	Portugal	Time-resolved fluorescence of tyrosine residues. a new tool to characterize protein conformational changes
ORLOVA Tatiana N.	Ukraine	Optical and spectral properties of liquid crystals with photosensitive chiral steroid dopant

PROTTI Stefano	Italy	Photoinduced arylation processes
SCHAFER Christian	Germany	Photoswitchable resorcin[4]arenes
SILVA Liana	Portugal	Nystatin and ceramide interaction with multicomponent model membranes: relating membrane biophysics with antibiotic action and apoptosis
SILVI Serena	Italy	Artificial molecular machines
VAYA PEREZ Ignacio	Spain	Excited states of the nonsteroidal anti-inflammatory drug flurbiprofen as probes for the interaction with proteins
WOLL Dominik Florian	Germany	New photolabile protecting groups with intramolecular sensitization - synthesis photokinetic characterization and application for DNA chip synthesis
ZHAO Yong Sheng	China	Preparation and optoelectronic of organic nanomaterials

ACTIVITIES OF NATIONAL GROUPS

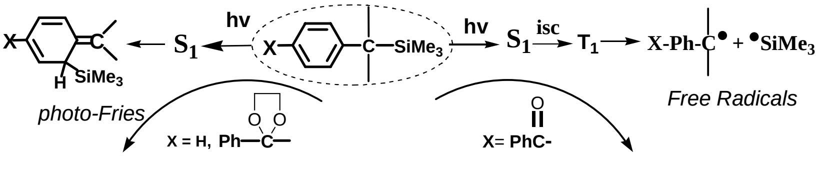
Photochemistry and Photophysics at the University of Ioannina, Greece

The *University of Ioannina* was founded in 1970 in the city of Ioannina (north-western Greece) and today includes 17 academic Departments with ca. 550 faculty members, 13.500 undergraduate and 3.500 postgraduate students.

Research activities in Photochemistry and Photophysics at the University of Ioannina take place mainly at the Departments of Chemistry and Physics and an impetus was given through the foundation of the Central Laser Facility of the University in 1999.

Organic Photochemistry, Free Radical Chemistry and Photopolymerizations
Dr. Antonios K. Zarkadis, Assoc. Professor
Dr. Michael G. Siskos, Assist. Professor
Department of Chemistry

Research activity is focused in understanding the mechanisms of basic photochemical reactions such as the ***photodissociation*** and ***photorearrangement*** in benzylic organic and organosilicon systems and particularly the role of *substituent effects* and *structure-reactivity relationships* hereupon. Substituents directly bound to the chromophore system often alter dramatically its reactivity as a consequence of the different electronic and spin configurations inherent in the involved excited states. Inversely, it is challenging to exploit the introduction of suitable substituents for a desirable



photochemical outcome. The photochemistry of benzyl silanes demonstrates such an example: the phenyl-chromophore leads *via* the **S_1** state to persistent *photo*-Fries rearrangement products, while introduction of the benzoyl group leads through an effective isc mechanism to the **T_1** state which finely dissociates to free radicals. It is just this effective photodissociation which renders *only* the benzoyl derivatives suitable photoinitiators in photopolymerization reactions.

The above studies are performed through: (**1**) the synthesis of suitable model compounds (*Organic Synthesis*) and traditional photoproduct analysis (UV, IR, NMR, MS, GC/MS, HPLC), and (**2**) steady-state and time-resolved spectroscopic methods (*EPR spectroscopy, emission and absorption spectroscopy, ns- and ps-laser flash photolysis*) for studying the relevant excited states S_1, T_1, free radicals and other reactive intermediates, (**3**) Computational photochemistry, and (**4**) photopolymerizations. Collaborations are established with Prof. O. Brede and Dr R. Hermann (University of Leipzig, Germany**),** Dr G. Gurzadyan (T. U. Munich, Germany), and Dr. M. Budyka, Russian Academy of Sciences, Chernogolovka-Russia.

Equipment: Standard organic photochemical laboratory and EPR Spectroscopy (Varian E100)

Selected Publications: (1) "Mechanism of the Photodissociation of 4-Diphenyl(trimethylsilyl)methyl-N,N-dimethylaniline" D.Tasis, M. G. Siskos, A. K. Zarkadis, S. Steenken, G. Pistolis*, J. Org. Chem. 53* (**2000**) *4274-80;* (2) S. Garas; M. G. Siskos, A.K. Zarkadis, "C-N vs. C-C bond photodissociation in N-(tert-butyldiphenylmethyl)aniline" *Int. J. Photoenergy*, 6 (**2004**) 233-240; (3) "Free Electron Transfer from Xanthenyl and Fluorenyl Silanes to Parent Solvent Radical Cations: Effects of Molecule Dynamics" , N. Karakostas, S. Naumov, M. G. Siskos, A. K. Zarkadis, R. Hermann and O. Brede*, J. Phys. Chem. A 109 (**2005**) 11679*; "Triplet vs. Singlet-state imposed photochemistry. The role of substituent effects on the photo-Fries and photodissociation reaction of triphenylmethyl silanes", A. K. Zarkadis et al., *Photochem. Photobiol. Sci. 4* (**2005)** 469; (4) M. G. Siskos, A. K. Zarkadis, Siskos MG, Zarkadis AK, Gritzapis PS, et al. "The photo-Fries rearrangement of 9-trimethylsilyl substituted xanthenes", *Photochem. Photobiol. A: Chem.* 182 (**2006)** 17.

Environmental Technology and Photocatalysis

Dr. Triantafyllos A. Albanis, Professor

Department of Chemistry

The aim of the research is to develop novel analytical methods for monitoring organic micropollutants in the environment as well as the development of techniques for the removal of toxic substances from water, soil and sediments.

Objectives: Environmental Chemistry of pesticides and related organic micropollutants, transportation of pesticides in environmental ecosystems, development of integrated analytical methods for pesticides, metabolites and related organic micropollutants determination in environmental compartments, aquatic organisms, agricultural and food products, photolysis and photocatalytic degradation of pesticides, pharmaceuticals and related organic micropollutants.

Infrastructure: Gas chromatograph-mass spectrometer (GC-MS) Shimadzu Q5000, Liquid chromatograph- mass spectrometer (LC-MS) Shimadzu, Two gas chromatographs, Shimadzu 14A with ECD-FTD and FTD-FID, HPLC Shimadzu with DIA and UV-Vis, Ionic chromatograph Shimadzu, Gas chrompatograph Varian 3300 with ECD, Spectrometer UV-Vis, Suntest system, Systems for SPE and SPME (Extractions Systems).

Selected Publications: (1) Konstantinou I.K., T.M. Sakellarides, V.A. Sakkas and T.Albanis (**2001**), "Photocatalytic degradation of selected s-triazine herbicides and organophosphorus insecticides over TiO_2 suspensions", Environ. Sci. Technol, 35, 398-405; (2) Goncalves C., A.Dimou, V.Sakkas, M.F.Alpendurada, T.A.Albanis, (**2006**), "Photodegradation of Quinalphos in different natural waters and soil matrices under simulated solar irradiation", Chemosphere, 64, 1375-1382.; (3) Sakkas V.A., I.K.Konstantinou, T.A.Albanis (**2006**), "Photochemical fate of organic booster biocides in the aquatic environment", Hdb Environ Chem, O, 171-200; (4) Calza P., V.A. Sakkas, C. Medana, C. Baiocchi, A. Dimou, D. Giokas, E. Pelizzetti, T. Albanis (**2006**) "Photocatalytic degradation of diclofenac over aqueous TiO2 suspensions", Applied Catalysis B: Environmental, **67**,197-205; (5) Sakkas V.A., K. Shibata, Y. Yamaguchi, S. Sugasawa, T. Albanis (**2007**) ''Aqueous phototransformation of zinc pyrithione Degradation kinetics and byproduct identification by liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry'', Journal of Chromatography A, 1144, 175-182.

Photophysics - The Central Laser Facility (CLF) of the University of Ioannina

Dr. Constantinos Kosmidis, Professor

Department of Physics

The *Central Laser Facility (CLF)* of the University of Ioannina was founded in 1999 and is equipped with two 5 ns Nd: YAG pumped dye lasers (λ=205-800nm) and one 35 ps Nd; YAG laser (λ=1064, 532, 355, 266 and 213nm). At the same time there are a number of available work stations, such as: high resolution reflector time-of-flight (TOF) mass spectrometer in conjunction with position sensitive detection, electrostatic spherical electron energy analyzer, Czerny-Turner spectrograph with an intensified CCD camera and an Electron Multiplying CCD camera, z-scan apparatus, a number of effusive (Knudsen cell, metal vapor beams, etc) and supersonic molecular beams.

Research topics of current interest:

Spectroscopy of atoms and molecules; molecular dynamics; interaction of molecules with strong laser fields; molecular alignment; phase sensitive coherent control; non linear properties of materials

Selected Publications:(1) Matenoglou GM, Evangelakis GA, Kosmidis C, et al. "Hybrid pulsed laser deposition of ti-cu-n ternary nitride thin films" *Rev. Adv. Mater. Sci.* 15, 38-43, **2007,** (2) Matenoglou G, Evangelakis GA, Kosmidis C, et al. « Pulsed laser deposition of amorphous carbon/silver nanocomposites » *Appl. Surf. Sci.* 253, 8155-8159, **2007,** (3) Patsalas P, Kaziannis S, Kosmidis C, et al. « Optimized pulsed laser deposition by wavelength and static electric field control: The case of tetrahedral amorphous carbon films" *J. Appl. Phys.* 101, Art. No. 124903, **2007** (4) Kaziannis S, Kosmidis C "Comparative study of multielectron ionization of alkyl halides induced by picosecond laser irradiation", *J. Phys. Chem. A* 111, 2839-2851, **2007**, (5) Kosmidis C, Kaziannis S, Siozos P, et al. "Molecular hydrogen ion elimination from alkyl iodides under strong laser beam irradiation" , Inter. J. Mass Spectr. 248, 1-8 , **2006.**

Photophysics - Molecular Physics
Dr. John G. Philis, Assoc. Professor
Department of Physics

The research interests are focused on studies regarding the nature of the valence and Rydberg excited states of fundamental organic molecules (on the size of acetone or benzene derivatives), their molecular conformations, internal top rotations, etc. The main technique used is resonance-enhanced multiphoton ionization (REMPI, R2PI for the case of 1+1 REMPI). Intense pulsed dye laser (nanosec pulse, visible or UV beam) interacts with jet-cooled molecules (supersonic molecular beam). A time-of-flight mass spectrometer is engaged in the system for studies of laser induced mass spectra/fragmentation.

The work is basically done in the Central Laser Facility of the University of Ioannina.

Selected Publications: (1) "Torsional features in the (3s)$S_1 \leftarrow S_0$ transition of N-methylpyrrole and $C_4D_4NCH_3$ " J.G. Philis, *J. Mol. Struct.*, 651-653, 567 (**2003**), (2) "The multiphoton ionization spectrum of jet-cooled pyrimidine in the 3p Rydberg ${}^3B_1(\pi^*,n)$ states", J. G. Philis, *J. Mol. Spectrosc.* 232, 26 (**2005**), (3) "Search for cyclopropylbenzene conformers by studying the $S_1 \leftarrow S_0$ electronic transition", J.G. Philis and S. Wategaonkar , *J. Mol. Struct.* 834-836, 109 (**2007**),. (4) An experimental and theoretical study of the $S_1 \leftarrow S_0$ transition of p-ethynyltoluene, J.G. Philis and V.S. Melissas, *J. Chem. Phys.* 127, 204310 (**2007**), (5) "Resonance enhanced multiphoton ionization spectra of jet-cooled methanol and ethanol" , J.G. Philis, *Chem. Phys. Lett.*, 449, 291 (**2007**).

Dr. Antonios K. Zarkadis, Assoc. Professor
University of Ioannina
Department of Chemistry
451 10 Ioannina – Greece
Tel. (+30 26510) 98379 Fax. (+30 26510) 98799 E-mail:
azarkad@cc.uoi.gr
http://www.uoi.gr/schools/chemistry/index.files/en/index.files/Page2718.htm

Austrian Section of EPA

Report of a new start in 2008

After some time of lower activities of EPA during the last few years a large boost has been started by Dr. Markovitsi from Paris. A lot of things have been reactivated or launched newly, e.g. the EPA newsletter, EPA web page and the reduced conference fees for EPA members (IUPAC Göteborg, Sweden in July/August). The situation in Austria was somehow similar. As the organizer of CECP in 2006 and 2008 I decided to bring new life into EPA in Austria. Therefore CECP in Bad Hofgastein is now the international photochemistry conference of the Austrian section of EPA with a huge success of the last meeting in February, 2008 (113 participants from 18 countries). A general meeting of EPA Austria was held on CECP 2008. The following persons have been elected:

Head of EPA Austria:	Stephan Landgraf, Graz University of Technology
Local Treasurer:	Günter Grampp, Graz University of Technology

EPA Austria will be organized as a local group of EPA. We will collect the regular EPA fee and transfer it annually to EPA. There are no additional local fees. Activities in Austria will be financed by sponsoring. The current list of members in Austria:

Stephan Landgraf (head), Graz University of Technology
Günter Grampp (treasurer), Graz University of Technology
Anne-Marie Kelterer, Graz University of Technology
Arnulf Rosspeintner, Graz University of Technology
Martin Knapp, University of Vienna
Günther Knör, University of Linz
Christine Onitsch (student), Graz University of Technology
Asim Mansha (student), Graz University of Technology
Sabine Richert (student), Graz University of Technology

General meetings will be held annually - at CECP in Bad Hofgastein and at the GÖCH (Austrian Chemical Society) meeting of the Physical Chemistry Group (next time 2009 in Innsbruck). This will ensure that the exchange in Austria will work on a regular basis. Soon a web page will be launched (www.ptc.tugraz.at/epa). This year there will be efforts to increase the number of EPA members in Austria and to connect all groups working in this field. Additionally there will be a collaboration with the Physical Chemistry Group of the GÖCH in order to improve the connection between European and Austrian organisations of similar interests.

Presentation of the representatives of EPA in Austria since 2008:

Stephan Landgraf

Ao. Univ. Prof., Dr. (since 2002)
Institute PTC
Graz University of Technology
Technikerstr. 4/I, A-8010 Graz

Research interests:
Photochemistry, Electrochemistry
Application of semiconductor light sources

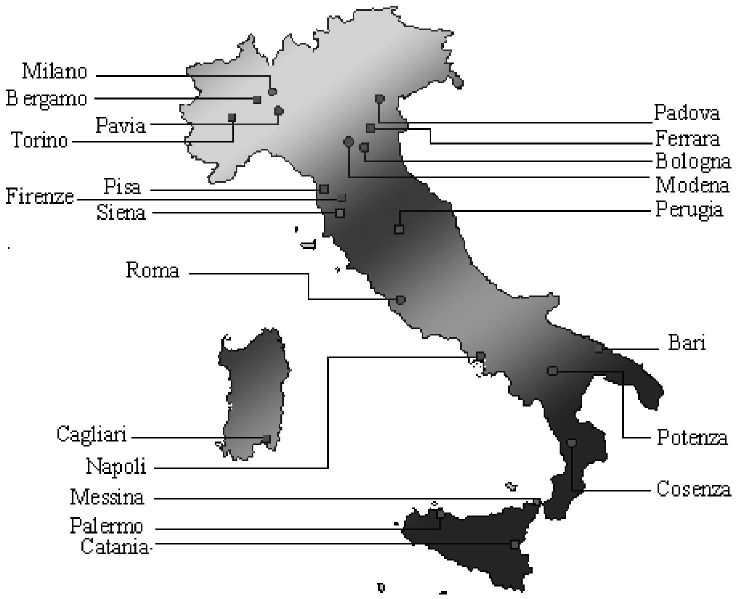
Günter Grampp

O. Univ. Prof., Dr. (since 1994)
Institute PTC
Graz University of Technology
Technikerstr. 4/I, A-8010 Graz

Research interests:
Electron transfer reactions
Photochemistry, EPR spectroscopy

Photochemistry in Italy

Last February, I addressed to the national photochemical groups afferent to the Italian Section of the EPA and some other groups that are known to be active in the study of the chemical and physical behaviour of electronically excited compounds (including also some photobiological groups), a circular letter asking for reports on their research activity. Even if practically all the contacted groups kindly sent their contributions, this survey does not pretend to be exhaustive and I apologize for unintentional omissions. The survey presented below describes the research lines in progress and the successful results. It is larger than foreseen and emphasizes the great interest deserved in Italy to photochemistry and strictly related fields. Compared with similar reviews published in the past, it appears that the level of photochemical research in Italy is quantitatively and qualitatively increased. While in the last decades the activity had been



mainly concerned with fundamental research, at present it is gradually moving towards new research lines with various approaches to potential applications, particularly in the fields of optoelectronics and biotechnologies.

Ugo Mazzucato
University of Perugia

University and CNR-Center of Bari

The photochemistry-related research topics in Bari were started in the late 1980s in a joint project launched by the Physical Chemistry group of the University of Bari and the CNR-Center for the light-matter interaction. The project led by Prof. Mario Della Monica (1932-2003) was initially focussed on the biophysics of the photosynthetic apparatus of anoxygenic photosynthetic bacteria.

Afterwards, several researchers joined the group and the scientific interests flourished to include oxygenic photosynthesis, cyclodextrin based supramolecular aggregates for environmental and health related issues, environmental application of photosynthetic micrograniisms and, most recently, nanocrystals and nanomaterials. In last fifteen years the group competences have vigorously grown and presently, under the direction of Prof. Angela Agostiano, ten permanent researchers, three lab technicians, ten post-docs and PhD students and numerous undergraduate students actively participate in the research. Furthermore, the group has reached a strong record of funding with several regional, national and European projects presently running.

Very recently the group has started projects on environmental related issues, tackling them with different approaches. Pollution abatement by eco-compatible and sustainable technologies is presently pursued in water by using

a) anoxygenic photosynthetic bacteria as tool for bioremediation of heavy metal polluted sites. Under photosynthetic condition purple bacteria are able to sequester and remove or detoxify heavy metal ions from fresh water bodies;
b) immobilized photosynthetic enzymes as biosensor for early warning herbicides contamination;

c) tailored nanomaterials – such as surfactant-capped ZnO nanocrystals or nanocrystalline catalysts (CdS/TiO_2) or novel semiconductor/metal hetostructures (TiO_2/Ag) – in the photodegradation of organic molecules;
d) supramolecular aggregates of cyclodextrin/photosynthetic pigments employed as photosensitizer against human pathologies.

Very recently investigations on the photoreaction of nephrotoxic mycotoxin (namely ochratoxin A) in cyclodextrin inclusion complexes have been also undertaken.

1. Dentuto, P. L.; Catucci, L.; Cosma, P.; Fini, P.; Agostiano, A.; D'Accolti, L.; Trevithick-Sutton, C. C.; Foote, C. S. J. "Effect of Cyclodextrins on the Physicochemical Properties of Chlorophyll a in Aqueous Solution" *J. Phys. Chem. B.*; 2005; **109**(3); 1313-1317
2. Milano F, Gerencsér L, Agostiano A, Nagy L, Trotta M, Maróti P. "Mechanism of quinol oxidation by ferricenium produced by light excitation in reaction centers of photosynthetic bacteria." *J Phys Chem B.*; 2007; **111**(16):4261-4270
3. R. Comparelli, E. Fanizza, M. L. Curri, P. D. Cozzoli, G. Mascolo, R. Passino, Agostiano "Photocatalytic Degradation of Azo Dyes by Organic-Capped Anatase TiO_2 Nanocrystals Immobilized onto Substrates" *Applied Catalysis B: Environmental* (2005) 55, 81-91.

University of Basilicata

The main research field of the photochemical group of Maurizio D'Auria and coworkers in Potenza (Basilicata) is "stereoselective photochemistry". Some general approaches to stereochemical control have been reported:

1. Photochemical reactions can be diastereoselective in the presence of a chiral carbon or restricting the possible movements of the molecule.
2. Photochemical reactions can be stereoselective by using chiral solvents or a chiral light or using chiral photosensitizers.

The Paternò-Büchi reaction is a [2+2]-cycloaddition reaction between a carbonyl compound and an alkene. We studied this reaction using furan derivatives as alkene. We studied the photochemical behavior in the presence of chiral auxiliaries on carbonyl compounds in zeolite and cyclodextrin,[1,2] using chiral carbonyl compounds,[3] and by using chiral furan derivatives.[4,5] In particular, we found that furan derivatives with a side chain with a hydroxyl group (2- or 3-furylmethanol derivatives) can give high diastereoselectivity: in this case the hydroxyl group drives the attack of the carbonyl group on a prochiral face of the furan ring; the most stable biradical intermediates thus obtained justify the observed diastereoselectivity.

1. D'Auria, M.; Emanuele, L.; Racioppi, R. *Photochem. Photobiol. Sci.* **2003**, *2*, 904.
2. D'Auria, M.; Emanuele, L.; Racioppi, R. *Lett. Org. Chem.* **2008**, in press.
3. D'Auria, M.; Emanuele, L.; Pace, V.; Racioppi, R. *Lett. Org. Chem.* **2006**, *3*, 350.
4. D'Auria, M.; Emanuele, L.; Racioppi, R. *Advances in Photochemistry,* Ed. By Neckers, D. C.; Jenks, W. S.; Wolff, T., John Wiley & Sons, Hoboken, NJ, Vol. 28, **2005**, p. 81.
5. D'Auria, M.; Emanuele, L.; Racioppi, R.; Valente, A. *Photochem. Photobiol. Sci.* **2008**, *7*, 98.

University of Bergamo

The research activity in the field of photochemistry carried out by the group of Tullio Caronna and coworkers at the Bergamo University in Dalmine, deals with the following lines:

1) synthetic organic chemistry: synthesis of azahelicenes. These compounds are intrinsically chiral, due to their helicity, and extensively conjugated. They show remarkable optical properties, such as very long triplet lifetimes. Azahelicenes with five or more fused aromatic rings, with one or more nitrogen atoms are being prepared, with synthetic methods which include photocyclization of precursors such as quinolylethenes or phenanthridyl-pyridyl-ethenes.

Azahelicenes can be quaternarized to prepare azahelicenium salts, whose optical properties and prospective applications are being explored. Different moieties can be introduced for this quaternarization, e.g. chiral groups, chains of different length and bulk or bearing end functionalities for tethering the helicene to a solid surface, etc.
Azahelicenes can be used for preparing complexes with metal ions, which may show, beside other properties, interesting non-linear optical behavior.

2) photocatalysis: TiO_2, in its different crystalline forms, is used, suspended in a solvent or deposited on a surface, both for catalysis of photochemical synthetic reactions exploiting sunlight for the functionalization of heterocycles, and for photodegradation of pollutants in air and water.

3) structural analysis: wide angle X-ray diffraction is used for the structural analysis of inorganic and organic powders. This analytical method is used, among other scopes, for the characterization of active materials for photocatalysis.

University of Bologna

Photochemistry and Supramolecular Chemistry Group

Nowadays, the research lines of this group at the Department of Chemistry "G. Ciamician" can be summarized as follows:

Mechanical nanomachines operated by light *(Vincenzo Balzani, Alberto Credi, Margherita Venturi, Serena Silvi, Matteo Amelia, Massimo Baroncini, Monica Semeraro)*
The bottom-up construction and operation of machines and motors of molecular size is a topic of great interest in nanoscience, and a fascinating challenge of nanotechnology. Like their macroscopic counterparts, nanoscale machines need energy to operate.[1] Although molecular motors of the biological world are fueled by chemical reactions, we and others have demonstrated that light energy can be used to power nanomachines by exploiting photochemical processes

in appropriately designed artificial systems. As a matter of fact, light excitation exhibits several advantages with regard to the operation of the machine, and can also be used to monitor its functioning through spectroscopic methods.[1] Recent results from our laboratory, in collaboration with other research groups in Italy and abroad, include a molecular elevator (Fig. 1a), an autonomous molecular shuttle powered by sunlight (Fig. 1b), and a piston-cylinder system operated by photoinduced proton transfer.[2,3] We are currently investigating the use of molecular machines to manipulate nanoparticles or to control bilayer membranes.

Photochemical devices for information processing *(Vincenzo Balzani, Alberto Credi, Serena Silvi, Matteo Amelia, Massimo Baroncini, Monica Semeraro)*

In living organisms information is processed, transferred and stored using molecular or ionic substrates. The design and construction of molecular systems capable of elaborating information could enable to carry out simple computing tasks not possible with silicon-based devices – e.g., in nanoscale spaces or *in vivo*.[1] In the long term, this research could lead to the development of a "chemical processor" based on radically new computing paradigms.

In our laboratory we have studied molecular and supramolecular systems capable of mimicking the function played by plug/socket and extension cable devices, and logic gates and circuits.[2,4] The latter systems exploit chemical or physical inputs and provide output signals according to programmed Boolean functions. We have shown that complex operations can be realized by means of the integration of basic functions within individual molecules. We have also realized molecular logic devices with all-optical inputs and outputs, based on the operation in series of distinct molecular switches that communicate with one another by the exchange of chemical signals.

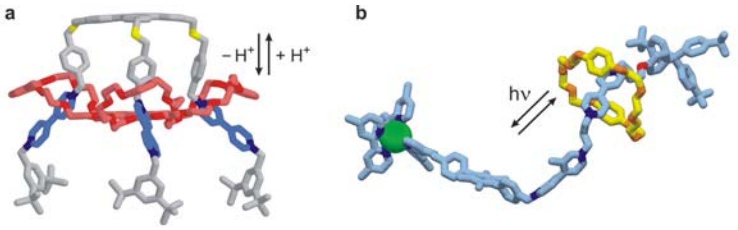


Fig. 1. (a) A molecular elevator operated by pH changes in solution. The motion of the red platform can be monitored by electrochemistry and absorption spectroscopy. (b) An autonomous molecular shuttle powered by sunlight. The motion of the yellow ring is followed by time-resolved absorption spectroscopy.

Fluorescent Chemosensors (*Luca Prodi, Nelsi Zaccheroni, Marco Montalti, Alberto Juris, Enrico Rampazzo, Sara Bonacchi, Riccardo Juris, Ettore Marzocchi, Damiano Genovese*)

The development of chemical sensors is dramatically changing the potentialities of chemical analysis. Chemical sensory devices have already found wide application in many fields, such as environmental monitoring, process control, food and beverage analysis, medical diagnosis, and, lately, in monitoring toxic gases and explosives for security reasons. Among the different chemical sensors, fluorescence-based ones present many advantages: fluorescence measurements are usually very sensitive, easily performed, versatile, and of low cost offering submicrometer spatial and submillisecond temporal resolution. A very fruitful approach recently followed by chemists for the design of new efficient chemical sensors is the supramolecular one, that typically entails the synthesis of molecules or supramolecules, conventionally referred to as chemosensors, containing a receptor unit and a so called "active unit", that is able to signal the interaction receptor-analyte with a significant change of one of its chemical physical properties. We have developed many fluorescent chemosensors for anions and metal ions both for biological (Fig. 2a) and environmental applications.[5,6]

Photo-active Nanoparticles (*Marco Montalti, Nelsi Zaccheroni, Luca Prodi, Alberto Juris, Enrico Rampazzo, Sara Bonacchi, Riccardo Juris, Ettore Marzocchi, Damiano Genovese*)
Nanoparticles have found many industrial employments in a wide range of fields such as electronics, optoelectronic, biomedical, pharmaceutical, cosmetic, catalytic, and materials areas, in products such as chemical-mechanical polishing, magnetic recording tapes, sunscreens, automotive products, catalyst supports, biolabels, electroconductive coatings, and optical fibres. In particular, the research in the field of photoactive nanoparticles aims to the development of innovative nanosystems for biological imaging, medical diagnostics, and therapeutics. In this context, we have developed a wide expertise in the synthesis and photophysical characterization of metals (gold[7], Fig. 2b, and silver) and silica nanoparticles[8] functionalized with suitable dyes, as labels for possible applications in the field of molecular biology. We are also able to synthesize and characterize 'mixed' nanoparticles, i.e., with a metal core and a silica shell, functionalized with luminescent moieties at different and selected distances from the core. In addition, we are also studying the possibility to obtain chemosensors based on nanoparticles, with the aim to obtain greater signal amplification effects.

Photoinduced energy- and electron-transfer processes in multicomponent systems *(Vincenzo Balzani, Paola Ceroni, Mauro Maestri, Margherita Venturi, Massimo Baroncini, Giacomo Bergamini, Carlo Giansante)*
Multicomponent supramolecular systems, in which light is employed to create and transport electronic energy, or to displace electrons from one molecular component to another, are interesting for their wide range of future applications, e.g. the development of antennas for light harvesting, molecular wires, and switches.

In this field we are currently investigating various types of dendrimers, which are well-defined macromolecules, exhibiting a tree-like architecture of nanodimensions, with peculiar chemical and physical properties. Since dendrimers can be functionalized with multiple photo- and electroactive groups in very close proximity,

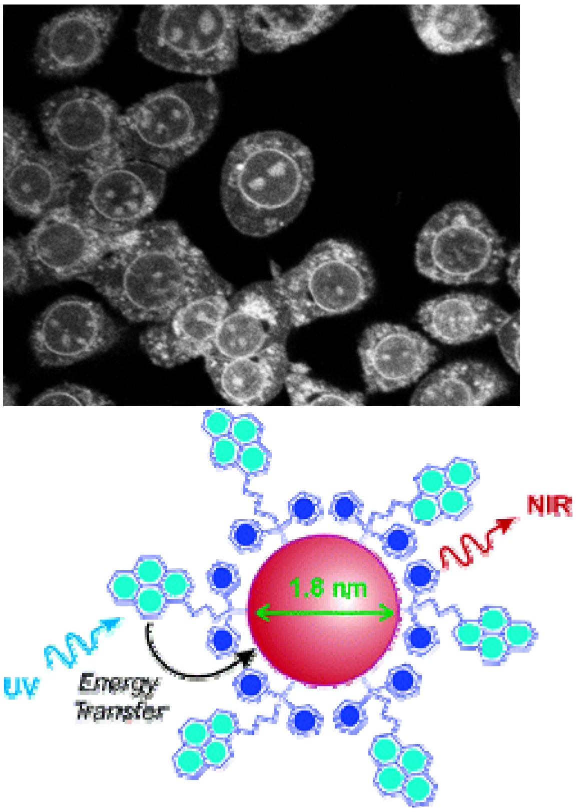


Fig. 2. (a) distribution of a Mg chemosensor in HC11 mouse mammary cells. (b) Schematic representation of enhanced sensitized NIR luminescence from gold nanoparticles via energy transfer from surface-bound fluorophores**.**

novel properties can indeed arise compared to the single chromophoric system. In particular, the investigation of dendritic structures functionalized with luminescent groups[9], photoswitchable units[10], energy and/or electron donor-acceptor components and the implementation of such functionalized dendrimers in devices, provide insight in the fundamental processes occurring in such complex systems and in their potential applications. Furthermore dendrimers, because of the capability of hosting in their three-dimensional internal cavities metal ions or even small molecules[11],

can find applications as sensors with signal amplification, carriers with controlled release and tunable antenna systems (Figure 3a).
Continuing our investigation on multicomponent systems, we have also studied heterodinuclear transition-metal complexes (Figure 3b), containing a shape-persistent phenylacetylene macrocycle as the bridging ligand, in which intramolecular energy- or electron-transfer processes occur with high efficiencies[12]. We are currently investigating systems based on a shape-persistent macrocycle similar to that shown in Figure 3b incorporating two different coumarins.

a **b**

M = Ru(II), Os(II), Os(III)

Fig. 3. Examples of the investigated multicomponent systems, in which intramolecular energy- or electron-transfer processes occur.

References

1) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines – Concepts and Perspectives for the Nano World, 2nd Ed.*, Wiley-VCH, Weinheim, 2008.
2) R. Ballardini, A. Credi, M.T. Gandolfi, F. Marchioni, S. Silvi, M. Venturi, *Photochem. Photobiol. Sci.* **2007**, *6*, 345, and references therein.
3) S. Silvi, A. Arduini, A. Pochini, A. Secchi, M. Tomasulo, F.M. Raymo, M. Baroncini, A. Credi, *J. Am. Chem. Soc.* **2007**, *129*, 13378.
4) B. Ferrer, G. Rogez, A. Credi, R. Ballardini, M.T .Gandolfi, V. Balzani, Y. Liu, H.-R. Tseng, J.F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 18411.
5) L. Prodi, *New J. Chem.* **2005**, *29*, 20.

6) G. Farruggia, S. Iotti, L. Prodi, M. Montalti, N. Zaccheroni, P. B. Savage, V. Trapani, P. Sale, F. I. Wolf, *J. Am. Chem. Soc.* **2006**, *128*, 344.
7) G. Battistini, P. G. Cozzi, J.-P. Jalkanen, M. Montalti, L. Prodi, N. Zaccheroni, F. Zerbetto, *ACS Nano*, **2008**, *2*, 77.
8) E. Rampazzo, S. Bonacchi, M. Montalti, L. Prodi, N. Zaccheroni, *J. Am. Chem. Soc.* **2007**, *129*, 14251.
9) P. Ceroni, G. Bergamini, F. Marchioni, V. Balzani, *Prog. Polym. Sci.* **2005**, *30*, 453, and reference therein.
10) F. Puntoriero, P. Ceroni, V. Balzani, G. Bergamini, F. Vögtle, *J. Am. Chem. Soc.* **2007**, *129*, 10714.
11) V. Balzani, G. Bergamini, P. Ceroni, F. Vögtle, *Coord. Chem. Rev.* **2007**, *251*, 325.
12) M. Venturi, F. Marchioni, B. Ferrer Ribera, V. Balzani, D.M. Opris, A.D. Schlüter, *ChemPhysChem* **2006**, *7*, 229.

Theoretical Photochemistry Group

Another group of the Department of Chemistry “G. Ciamician” of Bologna University is active in the field of theoretical photochemistry (G. Orlandi and M. Garavelli). The research interests include computational photochemistry and photobiology, with particular focus on the simulation of the reactivity of large molecules and the interactions between complex molecular systems and external stimuli such as photons. The aim is not to simply obtain a reproduction/interpretation of experimental data but to build predictive models and provide a deeper understanding of the phenomena that are investigated. Concurrently, the development of new tools for the exploration of potential energy surfaces and surface crossings in complex molecular architectures is pursued.

Active areas of research are: photobiology, for example vision and green fluorescent protein, photochromic materials and photochemically driven molecular switches, predictive models for the photo-reactivity of organic and biological system, photochemical processes in nano (e.g. supramolecular) structures, tuning and control of reactivity in organic chromophores, interactions with the environment.

- I. Conti, M. Garavelli, G. Orlandi,

"The Different Photoisomerization Efficiency of Azobenzene in the Lowest nπ* and ππ* Singlets: The Role of a Phantom State".
J. Am. Chem. Soc., 2008, 130, 5216-5230.

- I. Conti, F. Marchioni, A. Credi, G. Orlandi, G. Rosini, M. Garavelli
"Cyclohexenylphenyldiazene: a Simple Surrogate of the Azobenzene Photochromic Unit"
J. Am. Chem. Soc., 2007, 129, 3198-3210.
- P. Altoè, F. Bernardi, I. Conti, M. Garavelli, F. Negri, G. Orlandi
"Light driven molecular switches: exploring and tuning their photophysical and photochemical properties"
Theoretical Chemistry Accounts, 2007, 17, 1041-1059
- M. Garavelli
"Computational Organic Photochemistry: Strategy, Achievements and Perspectives"
Theoretical Chemistry Accounts, 2006, 116, 87-105.
- A. Cembran, F. Bernardi, M. Olivucci, M. Garavelli
"The retinal chromophore/chloride ion-pair: Structure of the photoisomerization path and interplay of charge transfer and covalent states"
Proceeding of the National Academy of Science USA, 2005, 102, 6255-6260.
- P. Altoè, F. Bernardi, A. Cembran, M. Garavelli, G. Orlandi and F. Negri
"Solvent effect on vibrational activity and photodynamics of the Green Fluorescent Protein Chromophore: a Quantum-Chemical Study".
J. Am. Chem. Soc., 2005, 127, 3952-3963.

CNR Institute for Organic Synthesis and Photoreactivity (ISOF), Bologna

Photophysical and photochemical studies of the ***Molecular Photoscience Group*** at ***ISOF*** (*http://www.isof.cnr.it/photoscience/*) focus on transition metal luminescent complexes, energy/charge transfer in supramolecular assemblies, electro-luminescent materials and drugs and drug–(bio)receptor systems. The activities can be resumed as follows:

Photo- and electro-active molecular arrays for light energy conversion

The scientific interests of *N. Armaroli and G. Accorsi* are concerned with photoinduced energy- and electron-transfer processes in supramolecular systems and nanostructures containing (i) fullerenes (ii) transition metal complexes (Cu, Ag, Au, Ru, Re, Os, Pt, Pd) (iii) aromatic conjugated oligomers (oligophenylenevinylene, oligophenylenethylene) (iv) porphyrins. The photochemistry and photophysics of luminescent materials such as rare earth emitters, d-block metal coordination compounds and organic fluorophores are also investigated in both liquid and solid phases, in connection with light energy conversion and lighting technologies. Unusual matrices, such as carbon nanotubes have also been employed to incorporate emitting materials via adsorption, covalent or non-covalent bonding.
The activity of *F. Barigelletti and A. Barbieri* focuses on the photophysical study of the excited states of d^6 transition metal coordination compounds (Ru, Rh, Re, Os, Ir and Pt) with polypyridyl or cyclometalated ligands, as potential photosensitizers in energy conversion systems (dye sensitised solar cells, and electroluminescent devices). They are also active in the field of photoinduced energy / charge transfer in supramolecular assemblies and study mainly organic (saturated and unsatured), inorganic and hybrid supramolecular systems of nanometer size. A variety of supramolecular systems containing photoactive and electroactive units, connected by covalently linked spacer, is investigated. Antenna-emitter complexes based on lanthanide centers, are studied as well. The mechanisms are elucidated also with the assistance of molecular modelling. These species have proved to be of use for the construction of photoactive molecular devices and as models for energy conversion and storage.
L. Flamigni and B. Ventura are active in the characterization of molecular architectures with potential application as antennas (light energy collectors) and charge separation (light energy conversion) devices. In these systems, the mechanism of wasting/conversion/storage of the light energy is fully elucidated. The structures, based on tetrapyrrole-type chromophores, aromatic bisimide, transition metal complexes, methyl viologens, and BODIPYs (as examples) are assembled both by covalent bonds and

by weak interactions and are designed in the frame of collaborations with a number of laboratories where the complex structures are synthesized.
The above described topics are studied within national and EU funded projects.

- N. Armaroli, G.Accorsi, D. Bonifazi, M. Prato, A. Parisini, M. Meneghetti and R. Marea, *Wet Adsorption of Eu(III)-complexes on Carbon Nanotubes Sidewalls,* Adv. Funct. Mater. **2007**, *17*, 2975–2982
- N. Armaroli, G. Accorsi, F. Cardinali, A. Listorti, *Photochemistry and Photophysics of Coordination Compounds: Coppe,* Top. Curr. Chem. **2007**, *280*, 69-115.
- L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Photochemistry and Photophysics of Coordination Compounds: Iridium,* Top. Curr. Chem. **2007**, *281*, 143-203.
- C. Sabatini, A. Barbieri, F. Barigelletti, K. J. Armb, J. A. G. Williams, *Fast, through-bond mediated energy transfer from Ir(III) to Ru(II) in di- and tetranuclear heterometallic assemblies: elucidation of a two-step Ir - Ir - Ru energy transfer process*, Photochem. Photobiol. Sci. **2007**, *6*, 397 - 405.
- L. Flamigni, E. Baranoff, J.-P Collin, J.-P Sauvage, *A Triad Based on an Iridium(III) Bis-Terpy Complex Leading to a Charge Separated-State with 120 ms Lifetime at Room Temperature,* Chem. Eur. J. **2006**, *12*, 6592-6606.

Electroluminescent organic devices

OLED architectures hosting newly synthesized metal complexes with high photoluminescence yields are studied by *V. Fattori and M. Cocchi* in order to achieve high electroluminescence efficiencies. In particular, third row transition metal and lanthanide complexes are used as emitting dopants in suitable host materials as their emitting triplets allow to harvest all the excited states resulting from the charge recombination events. Excited states dynamics and charge flow are investigated in order to obtain suitable matching of the electronic energy levels for each layer of a multilayer OLED assembly. Design and synthesis of different molecular structures for the luminescent compounds are developed with partners in collaborative project frames aiming to tune the colour of the light emitting device in the direction of different applications: displays, lighting, signals and signs.

- J. Kalinowski, M. Cocchi, D. Virgili, V. Fattori, J.A.G. Williams, *Mixing of Excimer and Exciplex Emission: A New Way to Improve White Light Emitting Organic Electrophosphorescent Diodes,* Adv. Mater. **2007**, *19*, 4000-4005.
- M. Cocchi, D. Virgili, V. Fattori, D. L. Rochester, J.A.G. Williams *N^C^N-Coordinated Platinum(II) Complexes as Phosphorescent Emitters in High-Performance Organic Light-Emitting Device,* Adv. Func.Mat. **2007**, *17*, 285-289.

Drugs and drug–(bio)receptor systems: spectroscopy, photochemistry *(Sandra Monti, Ilse Manet, Francesco Manoli)* and computational studies *(Giancarlo Marconi, Stefano Ottani)*

The non covalent binding and the photoreactivity of drugs complexed to artificial and natural receptors are currently studied in model systems for control of photoinduced side effects of drugs in pharmacological applications, development of new photoactivable therapeutic strategies and better understanding at the molecular level of the role of structural factors governing the drug-target interaction. Fluoroquinolones, non-steroidal antiinflammatory drugs, anthracyclines, antimalarials like Artemisinin and Chalcone derivatives interacting with proteins, nucleic acids and cyclodextrin-based carriers are presently under attention. Stability and spectroscopic features of the complexes are investigated using both steady state and time resolved absorption and emission techniques and circular dichroism. To gain knowledge on the photochemically generated intermediates and on their reactivity, transient absorption spectroscopy (with picosecond-to-millisecond resolution) and analytical techniques for determination of photoproducts are applied. Structural information about complexes in solution is achieved combining Molecular Mechanics and Molecular Dynamics calculations with the Quantum Mechanical calculation of the rotational strength, to be compared to the experimental ICD. With this approach difficulties in the achievement of X-ray structures or potential difference between solution and crystal conformation of drug:biomolecule complexes can be overcome. The group is also active in mechanistic photochemical studies, see, for example, the recent detection of cationic intermediates involved in the photodissociation of aloaromatics (Chem. Eur. J. 2008, 14, 10029-10039).

- S. Monti and S. Sortino, *Photoprocesses of non steroidal anti-inflammatory drugs within cyclodextrin cavities,* Chem. Soc. Rev. **2002,** *31*, 287-300**.**
- A. Albini and S. Monti**,** *Photophysics and Photochemistry of Fluoroquinolones,* Chem. Soc. Rev., **2003**, *32*, 238-250.
- G. Marconi, S. Monti, F. Manoli, A. Degli Esposti, A. Guerrini, *Circular-Dichroism studies on artemisinin and epiartemisinin and their β-cyclodextrin complexes in solution*, Helv. Chim. Acta **2004,** 87, 2368-2376.
- S. Monti, I. Manet, F. Manoli, M. L. Capobianco, G. Marconi, *Gaining an insight into the photoreactivity of a drug in a protein environment: a case study on nalidixic acid and serum albumin*, J. Phys. Chem. B, **2008**, DOI: 10.1021/jp711261n.

University of Catania

The current research activity of the **Group of Photochemistry and Photobiology** (S. Giuffrida, G. De Guidi and S. Sortino) at the Dipartimento di Scienze Chimiche encompasses multidisciplinary aspects of photochemistry covering the areas of *material chemistry* and *bio-pharmaceutical compounds.*

Material chemistry. This research activity is focused on the development of functional nanostructured materials in which the light plays a dominant role. Light in fact is a very appealing on/off trigger. Its peculiar features of environmentally friendly reactant, prompt availability and easiness of manipulation, associated to the fast response of many photochemical reactions, make the photo-controlled nanomaterials particularly fascinating for multifaceted applications in different fields encompassing molecular electronics and optoelectronics (*i.e.* photodiodes and photoswitches), environment (*i.e.* catalysts and sensors), biomedicine and pharmaceutics (*i.e.* photoactivated probes and drug delivery systems). Two main aspects have been developing at this regard. The first is focused on the preparation of “smart” thin films and nanoparticles able to perform specific functions upon the exclusive control of light stimuli. The second addresses the preparation of thin films and nanoparticles by using light as suitable reactant. The attention is paid mainly on thin film prepared by self-assembling, photochemical deposition by both vapour phase and liquid phase and Langmuir-Blodgett techniques, and on nanoparticles of metallic and amphiphilic nature.

***Bio-pharmaceutical compounds*.** This research activity is focused on the study of photophysical and photochemical processes of photosensitizing drugs in a variety of natural and artificial biological models of increasing complexity (*i.e.* nucleosides, native DNA, proteins, cellular membranes, cyclodextrins, micelles and vesicles), as well as on cells (fibroblasts) and on complex organisms (yeasts). The main aspects developed regard the characterization of the host-guest complexes, the elucidation of the photosensitizing effects and the development of biocompatible protective systems able to reduce the photoinduced damage. In this concern the attention is mainly focused on inclusion complexes and macroconjugates based upon natural and modified cyclodextrins, enzyme-like systems based on metal ions and their complex with biofunctional ligands, and natural antioxidant and their tailored derivative.

Representative references:

F. L. Callari and S. Sortino, *Chem. Commun.* 2008, DOI: 10.1039/b800132d

E. B. Caruso, S. Petralia, S. Conoci, S. Giuffrida and S. Sortino, *J. Am. Chem. Soc.* 2007, *129*, 480.

S. Sortino, S. Petralia, G. Compagnini, S. Conoci and G. Condorelli, *Angew. Chem. Int. Ed.* 2002, *41*, 1914.

F. L. Callari and S. Sortino, *J. Mater. Chem.* 2007, *17*, 4184.

E. B. Caruso, E. Cicciarella and S. Sortino, *Chem. Commun.* 2007, *47*, 5028.

F. Callari, S. Petralia and S. Sortino, *Chem. Commun.* 2006, 1009.

S. Giuffrida, G. Ventimiglia, S. Petralia, S. Conoci and S. Sortino, *Inorg. Chem.* 2006, *45*, 508.

S. Conoci, S. Petralia, P. Samorì, F. M. Raymo, S. Di Bella and S. Sortino, *Adv. Func. Mater.* 2006, *16*, 1425.

S. Giuffrida, G. G. Condorelli, L. L. Costanzo, I. L. Fragalà, G. Ventimiglia and G. Vecchio, *Chem. Mater.* 2004, *16*, 1260.

S. Monti and S. Sortino, *Chem. Soc. Rev.*,2002, *31*, 287.

A. Catalfo, C. Scifo, S. Stella, Marcella Renis and G. De Guidi, *Photochem. Photobiol. Sci.* 2005, *4*, 304 .
A. Catalfo, M. L. Calandra, M. Renis, M. E. Serrentino and G.De Guidi, *Photochem. Photobiol. Sci.* 2007, *6,* 181.

University of Ferrara

Three photochemistry groups are active in Ferrara.

The group led by Franco Scandola works in the domain of supramolecular photochemistry, with the aim of achieving basic knowledge on intecomponent energy and electron transfer processes and of emulating light-induced functions such as antenna effect, photoinduced charge separation, and light-induced switching. Both inorganic (transition metal complexes) and organic units (porphyrins, aromatic carboximides, diarylethenes) are used as molecular components. Fast (ns) and ultrafast (fs-ps) time-resolved spectroscopic techniques are extensively used. DFT and ab initio calculations are also implemented in support to the mechanistic studies.

- C. Chiorboli, M. T. Indelli, F. Scandola "Photoinduced Electron/Energy Transfer Across Molecular Bridges in Binuclear Metal Complexes" *Top. Curr. Chem.* **2005**, *257*, 63-102.
- F. Scandola, C. Chiorboli, A. Prodi, E. Iengo, E. Alessio "Photophysical Properties of Metal-Mediated Assemblies of Porphyrins" *Coord. Chem. Rev.*, **2006**, *250*, 1471-1496.
- M. T. Indelli, S. Carli, M. Ghirotti, C. Chiorboli, M. Ravaglia, F. Scandola "Triplet Pathways in Diarylethene Photochromism. Photophysical and Computational Study of Dyads Containing Ruthenium(II) Polypyridine and 1,2-bis(2-methylbenzothiophene-3-yl)maleimide Units" *J. Am. Chem. Soc.* **2008**, *130,* 0000.

The group led by Carlo Bignozzi is interested in the investigation of photoinduced electron transfer processes in inorganic coordination compounds, in functional nanomaterials and in extended solids. The overall goal of the research is to develop a molecular level understanding of chemical reactivity and excited state reactivity in homogeneous and heterogeneous environments important to material science and photochemistry. Practical applications of this research include solar energy conversion, chemical sensing, photocatalysis, design of nanomaterials for environmental decontamination, photochromic and electrochromic devices.

- Cazzanti,S.; Caramori,S.; Argazzi,R.; Elliott,C.M. and Bignozzi,C.A., "Efficient Non-Corrosive Electron-Transfer Mediator mixtures for Dye Sensitized Solar Cells". *J. Am. Chem. Soc.* **2006**, *128* (31), 9996-9997.
- C.A.Bignozzi, R.Argazzi, S.Caramori, " Energy and Inorganic Chemistry", in Inorganic and Bioinorganic Chemistry, edited by Ivano Bertini, in Encyclopedia of Life Supporting Systems (EOLSS), Developed under the Auspices of UNESCO, Eolss Publishers, Oxford, UK, **2007**, [http://www.eolss.net].
- Xue, D.; Elliott, C. M.; Gong, P.; Grainger, D. W.; Bignozzi, C. A.; Caramori, S, "Indirect Electrochemical Sensing of DNA Hybridization Based on the Cataltic Oxidation of Cobalt (II)". *J. Am. Chem. Soc.* **2007**, *129*(7), 1854-1855.

The group led by Andrea Maldotti is interested in photocatalysis. The final goal is the preparation and characterization of collectively organized inorganic systems able of catalysing selective oxidations with molecular oxygen. The photocatalytic materials employed are based on the use of polyoxoanions, metalloporphyrins (biomimetic catalysis) and inorganic semiconductors. Heterogenization of the photocatalysts is carried out with polymer matrices or nanostructured inorganic supports.

- A. Maldotti, A. Molinari, F. Bigi "Selective Photooxidation of Diols with Silica Bound $W_{10}O_{32}^{4-}$" *Journal of Catalysis* **2008**, *253*, 312.
- A. Molinari, G. Varani, E. Polo, S. Vaccari, A. Maldotti "Photocatalytic and Catalytic Activity of Heterogenized $W_{10}O_{32}^{4-}$ in the Bromide-assisted Bromination of Arenes and Alkenes in the Presence of Oxygen" *Journal of Molecular Catalysis A: Chemical* **2007**, *262*, 156.
- A. Maldotti, R. Amadelli, L. Samiolo, A. Molinari, A. Penoni, S. Tollari, S. Cenini "Photocatalytic Formation of Carbamate through

Ethanol-assisted Carbonylation of p-Nitrotoluene" *Chemical Communications* **2005**, 1749.

LENS - European Laboratory for Non-Linear Spectroscopy, Firenze

The investigation of the dynamical properties of molecular systems is one of the main research subjects at LENS since its establishment in 1989. The research is carried on by means of different time resolved optical techniques in which laser pulses as short as few tens of femtoseconds are used to characterize the spectral and dynamical properties of photoexcited molecular systems. In the past fifteen years, the scientific activity of the group has evolved into different branches which currently cover three major research areas:

- Ultrafast photochemical and photophysical processes in molecular systems
- Dynamics of biomolecules and photobiology
- Photoreactivity under high pressures

Transient absorption spectroscopy (TAS) is the main technique utilized to characterize the dynamical processes. However the group had developed in the years large competences in different branches of non-linear spectroscopy. The most recent developments have been in the field of two-dimensional IR spectroscopy, the vibrational counterpart of multidimensional NMR.

Ultrafast photochemical and phtophysical processes in molecular systems

In TAS, after the excitation of a molecular electronic state, a white-light continuum probe pulse is used to characterize at different delay times both spectral and dynamical features of the electronic states involved in the relaxation processes.

Inter- and intramolecular charge- and energy-transfer processes are ubiquitous in natural and artificial photochemically active systems. In order to better understand the behaviour of natural light-harvesting systems, the energy-transfer mechanisms active in synthetic dendrimer-like bicromophoric molecules are studied. As energy transfer processes are modulated by the molecular structure, the full spectral and dynamical characterization of different bichromophoric systems as a function of the bridge length and flexibility has been performed. An interesting family of bicromophoric compounds is based on an alizarine acceptor moiety, where the donor-acceptor energy transfer triggers an excited-state intramolecular proton transfer.

A deeper insight into the fast processes occurring in natural antennas is obtained by the dynamical characterization via TAS and fluorescence decay measurements of the electronic relaxation of free-base planar as well as diprotonated porphyrin. Indeed, the latter constitute a simple yet attractive system to investigate the influence of non-planarity on macrocycle photophysics.

Different classes of metal complexes are appealing as precursors for the realization of molecular scale devices. Molecular units whose magnetic properties can be light-controlled are interesting compounds in view of a possible application in the domain of information storage. An example of such molecules is constituted by cobalt complexes undergoing valence tautomeric interconversion, where an intramolecular electron transfer process can be induced by selective excitation of the charge-transfer transition.

Properly designed luminescent molecular chemosensors for metabolites in aqueous solutions are under study. Among these, the zinc(II) complex where a pentaamine chain is linked to a dipyridyl moiety is able to selectively bind and sense free uridine as well as two uridine-containing ribonucleotides. Both fluorescence decay and TAS measurements are used to characterize the exciplex emission due to the π-stacked complex arising from the dipyridine-uracyl interaction.

Dynamics of biomolecules and photobiology

Ligand photodissociation with short laser pulses in hemoproteins-ligand adducts is widely employed to unravel the elementary dynamical processes underlining the functional properties of proteins. The target of the investigations concerns the understanding of the protein functioning at the atomic level. The nature of the short lived intermediates generated immediately after photolysis represent the key point of the current research on hemoprotein dynamics. The recently discovered bacterial hemoglobins represent a most challenging class of proteins for studies of hemoproteins dynamics in view of their novel structural properties within the ever growing globin superfamily.

We recently investigated truncated hemoglobin from Bacillus subtilis and its CO complex with femtosecond time resolved transient absorption spectroscopy.
The idea to utilize localized vibrations such as Amide I mode in structural studies of polypeptides has been developing since ten years. The ambitious goal is to determine transient structures otherwise unobservable with intrinsically slow techniques such as NMR. At present only small polypeptides as long as some tens residues have been characterized by 2D-IR. However non-linear infrared spectroscopy is very promising in making possible the disentanglement of localized dynamical processes contribution to more complex dynamics.

Photoreactivity under high pressures

Solid state chemical reactions represent a challenging field in chemistry for the possibility to confine the reacting molecules and efficiently orient a reaction pathway as a result of both electronic density changes and geometrical constraints. At the ultrahigh pressures realized in a DAC (diamond anvil cell), the relative distances and orientations among the molecules are indeed defined and a selectivity can be introduced in the chemical reactions. Photochemical effects act at high pressure as a further effective regulatory tool of the reaction mechanism. The electronic distribution, and thus the molecular geometry, can be modified by a suitable optical excitation. The excited species can act as reaction initiator with the twofold effect of changing the pure pressure induced reaction pathway and lowering the reaction pressure making high pressure reactions an appealing preparation method also for large volume applications. Polymerization reactions have been successfully induced at few kilobars in several unsaturated systems and a high selectivity in the product as well as in the conformational properties have been obtained in the synthesis of important polymers such as polyethylene and polybutadiene. The possibility to appropriately and simultaneously control pressure, temperature and electronic excitation, opens new perspectives in solid state chemistry overcoming some of the ambient pressure limits, represented mainly by the possibility to induce a chemical reaction only in very complex molecules, and, more generally, in the synthesis of materials of technological interest by using only physical methods.

- The ultrafast energy transfer process in Naphtole - Nitrobenzofurazan bichromophoric molecular systems. A study by femtosecond UV-VIS pump-probe spectroscopy
Pier Luigi Gentili, Martina Mugnai, Laura Bussotti, Roberto Righini, Paolo Foggi, Stefano Cicchi, Giacomo Ghini, Simone Viviani, Alberto Brandi
Journal of Photochemistry & Photobiology, A: Chemistry 187 (2007) 209
- Unusually strong H-bonding to the heme ligand and fast geminate recombination dynamics of the carbon monoxide complex of Bacillus subtilis truncated hemoglobin.
Alessandro Feis, Andrea Lapini, Bruno Catacchio, Silvia Brogioni, Paolo Foggi, Emilia Chiancone, Alberto Boffi and Giulietta Smulevich
Biochem. 47 (2008) 902
- Excited-state absorption and ultrafast relaxation dynamics of porphyrin, diprotonatedporphyrin, and tetraoxaporphyrin dication
Agnese Marcelli, Paolo Foggi, Laura Moroni, Cristina Gellini, Pier Remigio Salvi
J. Chem. Phys. A 112 (2008) 1864
- Laser-induced selectivity for dimerization versus polymerization of butadiene under pressure
Margherita Citroni, Matteo Ceppatelli, Roberto Bini, Vincenzo Schettino
Science 295 (2002) 2058
- Laser-assisted high pressure chemical reactions
Roberto Bini
Acc. Chem. Res. 37 (2004) 95

University of Messina

The main research field of the group of Sebastiano Campagna and coworkers at the Department of Inorganic, Analytical and Physical Chemistry is the design of luminescent and redox-active multicomponent (supramolecular) species based on transition metal polypyridine complexes and the study of their photophysical properties and redox behavior, including intercomponent photoinduced energy and electron transfer processes. Ultimate objectives are devoted to the field of the photochemical conversion of solar energy (artificial photosynthesis).

Within this general frame, the team has been involved, in collaboration with the Balzani's team in Bologna, in the design of artificial antenna systems made of multimetallic dendrimers (mainly with Ru(II) and Os(II)-based components) capable to perform efficient photoinduced energy transfer among the individual subunits of the assemblies. Recently, the team has investigated in further detail the rate constants and mechanisms of the intra-dendrimer intercomponent energy transfer processes and found, by a series of collaborations involving teams of Ferrara, Lund, and Uppsala, that the energy migration processes in such dendrimers can occur in the femtosecond regime, sometimes also faster than energy migration in natural systems.

Beside the design of the artificial antennae described above, the team is also interested in the design of other components of a complete artificial photosynthetic process and is studying the functional integration of these components. To this scope, antenna dendrimers have been coupled to electron donor species such as phenothiazine groups, to prepare coupled antenna-reaction center systems. The light absorbed by the dendrimer unit has been converted into charge separation with quantitative yields, however the lifetime of the charge separated species is unsatisfactory. Work is in progress to improve this latter property of the systems.

For achieving an artificial photosynthesis a crucial point is also the development of charge pool systems: at this regard the team studied dinuclear Ru(II) containing specific sites capable to reversibly collect, upon successive photoinduced processes, up to four electrons.

The team has also investigated dendrimers based on organic chromophores and the photoinduced processes occurring in bichromophoric species containing Ru(II), Pt(II), or Ir(III) polypyridine species coupled with organic chromophores like anthracene, pyrene, dipyrromethene-BF_4 dyes and C_{60}. Among the most interesting results obtained in these studies are: prolongation of MLCT emission lifetime thanks to interchromophoric excited-state equilibration; fully characterization (spectrum and lifetime) of the phosphorescence of dipyrromethene-BF_4 and substituted fullerene subunits.

Finally, luminescent sensors (even in the solid state and with regard to gaseous substrates) and electronic coupling in molecular wires have been recently studied.

Selected references

- V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.*, **1998**, *31*, 26.
- R. Konduri, H. Ye, F. M. MacDonnell, S. Serroni, S. Campagna, K. Rajeshwar, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3185.
- J. Andersson, F. Puntoriero, S. Serroni, A. Yartsev, T. Pascher, T. Polivka, S. Campagna, V. Sundström, *Chem. Phys. Lett.*, **2004**, *386*, 336.
- F. Puntoriero, F. Nastasi, M. Cavazzini, S. Quici, S. Campagna, *Coord. Chem. Rev.*, **2007**, *251*, 536.

University of Milano

The research group at the Department of Physical Chemistry and Electrochemistry [team leader: Elena Selli (*elena.selli@unimi.it*)] is active in the following topics.

After having investigated the mechanism of photoinduced polymerization and grafting of polyfunctional monomers on polymeric substrates and on the photoreactivity of benzylidene compounds and azo dyes in solution, in the last decade the research interest of the group has been mainly centred on the mechanistic aspects of photocatalysis on semiconductors. Starting from kinetic investigations on the effects of humic substances on the redox processes occurring under solar irradiation in aquatic systems containing semiconductor oxides able to act as photocatalysts [1], the attention has been mainly focused on the electron transfer processes occurring at the semiconductor-aqueous solution interface under irradiation and on the active species so produced [2]. The effects induced by surface and bulk modifications of the photocatalysts on the oxidative photocatalytic degradation of water pollutants have been studied in detail, also when photocatalysis is employed in combination with other advanced oxidation processes for water de-pollution. Finally, the photocatalytic splitting of water for hydrogen production is being investigated employing different experimental setups [3].

1. E. Selli, V. Eliet, M.R. Spini, G. Bidoglio:

   Effects of Humic Acids on the Photoinduced Reduction of U(VI) in the Presence of Semiconducting TiO_2 Particles,

   Environ. Sci. Technol. **34** (2000) 3742.

2. M. Mrowetz, E. Selli:

   Enhanced photocatalytic formation of hydroxyl radicals on fluorinated TiO_2,

   Phys. Chem. Chem. Phys. **7** (2005) 1100.

3. E. Selli, G.L. Chiarello, E. Quartarone, P. Mustarelli, I. Rossetti, L. Forni:

   A photocatalytic water splitting device for separate hydrogen and oxygen evolution,

   Chem. Commun. (2007) 5022.

University of Milano-Bicocca

The research activity in the field of photocatalysis of the group at the Department of Materials Science (F. Morazzoni and R. Scotti) concerns the following topics:

1) Synthesis of nanosized TiO_2 powders with controlled morphology, particle size and shape, crystalline phase composition, by means of different preparation methods (hydrothermal[a], surfactant assisted sol-gel [b]).
2) Correlations between the photocatalytic activity of TiO_2 with different oxidative agents (H_2O_2, O_2) and phase composition, morphology and structure of the oxide.
3) Electron Paramagnetic Resonance (EPR) study of the species involved in the photocatalitic processes and their relations with the catalyst efficacy: a) electron and hole trapping centers (Ti^{3+}, O^- and O_2^-) in UV irradiated TiO_2 ; b) short-lived $OH^\bullet$ radicals, UV generated in the presence of the oxidant agent, detected by spin-trapping technique.

a) A.Testino, I. R. Bellobono,V. Buscaglia, C. Canevali, M. D'Arienzo, S. Polizzi, R. Scotti, F. Morazzoni, *Optimizing the photocatalytic properties of hydrothermal* TiO_2 *by the control of phase composition and particle morphology. A systematic approach*, *J. Am. Chem. Soc,* *129, 3564 (2007)*
b) R. Scotti, I.R. Bellobono, C.Canevali, C. Cannas, M. Catti, M.D'Arienzo, A.Musinu, S. Polizzi, M. Sommariva, A.Testino, F. Morazzoni, *Sol-gel pure and mixed-phase titanium dioxide for photocatalytic purposes. Relations between phase composition, catalytic activity and charge trapped sites, Chem. Mater. (2008) in press.*

University of Modena and Reggio Emilia

The spectroscopy and photophysics group at the Chemistry Department in Modena has recently performed both theoretical and experimental research along the following lines:
- Photo-induced processes in molecules and molecular aggregates (F. Momicchioli, G. Ponterini, D. Vanossi, I. Baraldi): this is a classical research area of the group in which calculation and experiment have often been synergically integrated. Recently investigated problems include the photophysics/chemistry of merocyanines, squaraines, curcumins and single-molecule magnets; the fluorescence solvatochromism of merocyanines; the excitation energy transfer (EET) in cyanine/oxonol ion pairs;
- Materials and devices for photonic applications (F. Momicchioli, G. Ponterini, D. Vanossi): investigation, both quantum-chemical and spectroscopic, of the potential of merocyanines and J-aggregated cyanines as non-linear-optical (NLO) chromophores; build-up by spin-coating, Langmuir-Blodgett and layer-by-layer (LBL) approaches of films containing chromophores of photonic relevance (polythiophenes, J-aggregated cyanines, merocyanines) and investigation of their structural and functional (luminescence and NLO) properties;
- Environmental photochemistry (M. Caselli, G. Ponterini): identification of products and analysis of mechanistic aspects of the photodegradation of sulfonylurea herbicides in environmentally significant conditions.

New research topics, on which work has been done in the last two years, are:

- Spectroscopy and photophysics of bio-molecules of pharmaceutical relevance (G. Ponterini): spectroscopic/photophysical investigation of i) EET in model oligopeptides; ii) interaction of EC thymidilate synthase (TS) with a prototype inhibitor. Within the LIGHTS project (6th EFP, *http://www.lights-eu.org*) several problems involving human TS and its inhibitors (e.g., protein dimerisation equilibrium, peptide conformation) are currently being investigated;
- Luminescent materials for environmental applications (M. Caselli, G. Ponterini): LBL films containing luminescent polymers, monomeric and J-aggregated dyes are characterized both structurally and functionally as sensors of environmentally significant chemical species. Composite materials with integrated electrochemical/luminescent properties are being designed for environmental applications;
- Structures, spectra and photophysics of new organic fluorophores (I. Baraldi): new organic fluorophores derived from di(styryl)heterocycles are synthesized and their rotational isomerism, absorption and fluorescence spectra and photophysic are investigated experimentally and theoretically. The new fluorophores may find application as fluorescent probes, dye laser media, scintillators and as π-core for new push-pull polyenes.

University of Napoli

The research group of Maria Rosaria Iesce (*iesce@unina.it*) at University of Naples Federico II (Department of Organic Chemistry and Biochemistry) has a long standing experience in the field of organic photochemistry. In particular, the research activity is aimed at developing novel synthetic procedures for oxygenated compounds of wide interest based on the dye-sensitized photooxygenation of heterocycles (oxazoles, furans, 1,4-oxathiins, 1,4-dithiins). At the moment, the research is directed to use glycosyl furans as starting heterocycles for the synthesis of functionalized *O*- or *C*-glycosides and *C*-nucleosides. Among the others, novel pyridazine, pyrazoline and bis-epoxide *C*-nucleosides have been prepared, all compounds of pharmacological interest.

Currently the group is also investigating the photochemical behaviour of some xenobiotics (the most used drugs and pesticides) under environmental-like conditions, with particular attention to the isolation and characterization of photoproducts. Nowadays there is a great concern about the risk associated with the introduction of xenobiotics into the aquatic environment since their transformation and degradation products (environmental metabolites) can be more noxious than the parent compounds.

University of Padova

Laboratory of Medical and Environmental Photobiology

The research activity of this laboratory (led by Giulio Jori) at the Department of Biology can be thus summarized.

1. Porphyrin-photosensitised processes: studies at a basic and cellular level. Applications for the photodynamic therapy of tumours.

The mechanisms controlling the efficacy of porphyrin-photosensitised processes are studied in both model systems (e.g. liposomes, lipoproteins, isolated mitochondria) and cell cultures. Particular attention is focused on the introduction of chemical features into the tetrapyrrolic core which promote the association of the porphyrin with pre-selected subcellular sites. Toward this aim, the degree of hydrophobicity/hydrophilicity of the porphyrin molecule is modulated by (a) the modification of the size or the nature of the macrocycle (e.g., moving from porphyrins to porphycenes, chlorins or phthalocyanines); (b) the attachment of functional groups in the peripheral position with the goal to generate amphiphilic derivatives; (c) the insertion of penta- or hexa-coordinated metal ions at the centre of the macrocycle thus taking advantage of the possibility to fine tune the chemical properties through the addition of one or two axial ligands. The achievement of different patterns of photosensitiser distribution among the various subcellular compartments allows the development of a variety of reaction pathways, leading to different kinetics and mechanisms of cell photoinactivation. This is a basic requirement for obtaining a close control of the photoprocesses occurring in complex biological

systems, including cells and tissues. Novel perspectives are opened by the use of porphyrin-loaded gold or silica nanoparticles coupled with targeting agents for selected receptors which are preferentially expressed at the surface of malignant cells.These investigations are also exploited to *in vivo* levels for performing pharmacokinetic and phototherapeutic investigations in experimental animal models carrying subcutaneously transplanted in order to develop improved protocols for the photodynamic therapy of tumours.
This research line is developed in collaboration with Prof. A. Villanueva from the Universidad Autonoma de Madrid (Spain).

2. Photosensitised inactivation of microbial cells: applications for the treatment of infectious diseases and addressing environmental problems.

Bacterial and fungal cells are poorly responsive to photosensitisation owing to the presence of an outer wall with a tight three-dimensional architecture. We have engineered some cationic porphyrins, which bring about a very fast binding with the array of negative charges at the surface of the outer wall and, upon photoactivation by visible light wavelengths, induce the irreversible photooxidation of specific wall constituents (e.g., peptidoglycans); the permeability of the wall is increased and significant concentrations of the porphyrin can reach inner cell districts and induce cell death. The understanding of the main aspects of such a mechanism led to the development of protocols for a highly selective killing of microbial cells as compared with the components of potential host tissues. A particularly efficient tetra(N-methyl-pyridyl)Zn(II)-phthalocyanine was identified, which went favourably through the toxicological tests and is now in clinical trials for the treatment of chronic wounds, periodontal diseases and oral candidosis.

The photodynamic technique appears to be endowed with several favourable features, such as (a) the broad spectrum of action, since one photosensitiser and one irradiation protocol allow an extensive (4-6 log) decrease in the population of different microbial pathogens, including Gram-positive and Gram-negative bacteria, yeasts, mycoplasmas and fungi; (b) the efficient photoinactivation of both wild and antibiotic-resistant microbial strains; (c) the lack of selection of photoresistant bacterial or fungal cells; and (d) the very low risk of inducing mutagenic effects.

Recent developments suggest the possibility to extend this technique also treatment of infectious diseases in the veterinary field. Moreover, the ascertained photosensitivity also of parasitic protozoa prompted the use of this technique for an environmentally friendly disinfection of waters from fish-farming plants and the protection of biodiversity, especially as regards the conservation of some amphibian species which are under serious threat of extinction owing to attack from water-borne fungal, parasitic and bacterial pathogens.

This research line is developed in collaboration with the company Molteni from Firenze (Italy). Collaborations are also activated with the Istituto Agrario San Michele all' Adige (Trento) and the Parco "Natura Viva" (Bussolengo, Verona)

3. Photothermal sensitisation and its potential for the photothermal therapy of tumours.

Photothermal sensitisation is based on the presence of molecular absorbers whose radiationless decay to the ground state occurs on a picosecond time scale; the use of laser sources operated in a pulsed regime at high fluence rates (e.g., 1 Jcm^{-2}) creates the conditions for the generation of high temperature spikes in the microenvironment of the photosensitiser (ca. 3 nm sphere) and the consequent setting up of acoustic shock waves causing both mechanical and chemical damage to a cell or tissue. These effects are potentiated in biological systems when the photosensitisers are present at high local concentrations due to aggregation or compartmentalisation with simultaneous generation of two or more thermal spikes in close proximity. These processes have been tested in our laboratory at a cellular level and found to be successfully promoted by several dyes, including azo-dyes, triphenylmethane derivatives, porphyrins coordinated with transition metal ions and cyanines. The availability of photothermal sensitisers which show a high affinity for experimental tumours, e.g., Ni(II)-naphthalocyanines or selected cyanines, opens the possibility to use this approach for a novel treatment of neoplastic diseases, termed photothermal therapy (PTT), as confirmed by preliminary *in vivo* studies with tumour-bearing mice. Interestingly, photothermal processes can be promoted by irradiation in the 900-1000 nm spectral region, where light penetration into human tissues is maximal, and efficiently occur also in the absence of oxygen: hence, PTT could be very useful for the treatment of poorly vascularized tumours.

This research line is developed in collaboration with Prof. M.A.J. Rodgers from the University of Ohio at Bowling Green (USA), as well as with Prof. L. Prodi from the University of Bologna and the company Cyanagen from Bologna (Italy)

Selected references

1 G. Jori, O. Coppellotti
Inactivation of pathogenic microorganisms by photodynamic techniques: mechanistic aspects and perspective applications
Anti-Infective Agents in Medicinal Chemistry 6:119-131 (2007)

2 M. Magaraggia, F. Faccenda, Gandolfi A., G. Jori
Treatment of microbiologically polluted aquaculture waters by a novel photochemical technique of potentially low environmental impact.
J. Environ. Monit. 8: 923-931 (2006)

3 M. Camerin, S. Rello, A. Villanueva, X. Ping, M.E. Kenney, M.A.J. Rodgers, G. Jori
Photothermal sensitisation as a novel therapeutic approach for tumours: studies at a cellular and animal level.
Eur. J. Cancer, 41:1203-1212 (2005)

Photochemistry and Photobiology of Drugs

Since decades, this research group, led by Francesco Dall'Acqua, at the Department of Pharmaceutical Sciences, is skilled in the synthesis and evaluation of the mechanism of action of photochemotherapeutic drugs. The photobinding of many psoralen derivatives and analogues towards bio(macro)molecules such as unsaturated lipids and nucleic acids has been extensively studied with the aim of understanding the molecular basis of their efficacy and improving the clinical effectiveness of PUVA (Psoralen + UV-A light) therapy.

A new type of photochemotherapy has been proposed for the treatment of thalassemia using apheresis, isolating erythroid stem cells, irradiating them with psoralen then subsequent reinfusion [Italian Patent Appl.]. This treatment photoinduces erythroid differentiation, induction of γ-globin mRNA and enhancing γ-globin synthesis and haemoglobin [European Patent Appl.; *Biochem. Pharmacol.***75**, 810 (2008)].

The photolysis of psoralens has also been considered and it has been shown that a photolyzed solution of psoralens retains some of the activities of the PUVA treatment. On one side, it induces apoptosis in selected cell lines [*Blood* 109, 4988 (2007)], thus suggesting a possible new mechanism for explaining the efficacy of photopheresis against lymphomas and organ rejection. On the other hand, the mixture of photoproducts is also able to induce erythroid differentiation as PUVA does. The research is now dealing with the identification of which photoproduct/s is/are responsible for these actions, among the numerous formed by UVA irradiation of psoralens.

Research studies have also been performed and are in progress on several classes of drugs such as fluoroquinolone antibiotics, antidepressants, anti-inflammatory agents, antimalarials, etc. The photostability is studied in solution and in pharmaceutical formulations, in order to identify the photoproducts and the mechanisms through which they form. Furthermore, experiments with biomolecules are carried out and phototoxicity is assessed in various cell lines [*Chem. Res. Toxicol.* **19**, 156 (2006); *Photochem. Photobiol.* **83**, 1415 (2007)].

A further topic is represented by new penta-and hexacyclic derivatives of quinolizinium ion as DNA-binding and DNA–photocleaving compounds. These molecules, termed photonucleases, operate through distinct mechanisms. A class of compounds photoinduce the formation of reactive species, such as singlet oxygen or the hydroxy radical, that damage DNA. In a second class, the photonuclease is bound to nucleic acid before its activation by light and DNA damage is localized at or near the binding site. These compounds, like any other small DNA-binding molecule, undergo complexation by intercalation or by fitting into the minor groove of the DNA. Thus, the photosentized damage to DNA can be applied as a phototherapeutic approach [*J. Org. Chem.* **71**, 8401 (2006)].

University of Palermo

"Schiavello-Grillone" Photocatalysis Group

This research group [coordinated by Vincenzo Augugliaro (*augugliaro@dicpm.unipa.it*) and Leonardo Palmisano (*palmisano@dicpm.unipa.it*); coworkers: Agatino Di Paola, Giuseppe Marcì, Vittorio Loddo, Elisa García-López, Maurizio Addamo, Marianna Bellardita, Giovanni Palmisano, Sedat Yurakal] at the "Dipartimento di Ingegneria Chimica dei Processi e dei Materiali" works on the following fields:

1) Preparation and characterisation of photocatalysts (mainly TiO_2) through sol-gel methods starting from inorganic and organic precursors; a particular care has been devoted in studying the influence of preparation method on the TiO_2 phases obtained;
2) Reactivity of photocatalytic powders in liquid-solid and gas-solid regimes, by using inorganic and organic species as substrates; in particular pharmaceuticals have been also degraded.
3) Immobilization of TiO_2 (anatase, rutile and brookite phases) thin films over glass slides, glass beads and polymeric materials, by using dip- and spin-coating; influence of thermal treatment temperature and precursors on films properties;
4) Photocatalytic oxidation of alcohols to aldehydes in aqueous solvents by using highly selective home-prepared catalysts; in particular the parameters influencing the process selectivity have been deeply investigated;
5) Photocatalysis coupled to other technologies, such as ozonation, electrochemistry, biological treatments;
6) Modelling of radiation field in fixed-bed photocatalytic reactors; semi-experimental methods for the determination of quantum yield, as a method to characterise catalysts;
7) Study of photocatalytic reactions kinetics, through Langmuir-Hinshelwood model, and incorporation of the radiation field model into the kinetic one.

Recent Publications

1) G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, E. García-López, V. Loddo, L. Palmisano, *Influence of the Substituent on SelecitvePhoto-catalytic Oxidation of Aromatic*

Compounds in Aqueous TiO_2 Suspensions, Chem. Commun. 2006 pp. 1012-1014

2) V. Augugliaro, M. Litter, L. Palmisano, J. Soria, *The Combination of Heterogeneous Photocatalysis with Chemical and Physical Operations: a Tool for Improving the Photoprocess Performance,* J. Photochem. Photobiol. C: Reviews 7 (2006) pp. 127-144
3) G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, A. Di Paola, E. García-López, V. Loddo, G. Marcì, L. Palmisano, M. Schiavello, Selectivity of Hydroxyl Radical in the Partial Oxidation of Aromatic Compounds in Heterogeneous Photocatalysis, Catal. Today 122 (2007) pp. 118-127
4) S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro, L. Palmisano, *Nanostructured Rutile TiO_2 for Selective Photocatalytic Oxidation of Aromatic Alcohols to Aldehydes in Water*, J. Am. Chem. Soc. 130 (5) (2008) pp.1568-1569
5) M. Addamo, V. Augugliaro, A. Di Paola, E. García-López, V. Loddo G. Marcì, L. Palmisano, *Photocatalytic Thin Films of TiO_2 Formed by Sol-Gel Process Using Titanium Tetraisopropoxide as the Precursor,* Thin Solid Films 516 (2008) 3802-3807

Organic Photochemistry Group

Another research group active in the field of photochemistry in Palermo is the Organic Photochemistry Group (coordinated by Nicolò Vivona) at the Department of Organic Chemistry. The research is mainly focused on the photochemistry of heterocycles. Other studies regarded the photoreactivity of diterpenes, the photoinduced cross-linking of polymers and intrazeolite photochemistry.

The photoreactivity of 1-oxa-2-azoles has been investigated with a particular interest on the transformation into other heterocyclic systems. For instance, the photochemistry of acylamino-1,2,5-oxadiazoles has been used for the synthesis of 3-amino-1,2,4-oxadiazoles. In its turn, the photoreactivity of 1,2,4-oxadiazoles has been thoroughly investigated. After cleavage of the O-N bond, the photolytic intermediate can evolve towards the formation of reduction or solvolysis open-chain products or, in the presence of sulfur or nitrogen nucleophiles, of thiadiazoles and triazoles. Other photochemical pathways accessible to the 1,2,4-oxadiazole are: the *Internal Cyclization – Isomerization (ICI)* into 1,2,4-oxadiazole regioisomers, the *Ring Contraction – Ring Expansion (RCRE)* into 1,3,4-oxdiazoles, the *Migration – Nucleophilic Attack – Cyclization (MNAC)* into 1,2,4-triazoles, the *Photoinduced Electron Transfer (PET)* leading to quinazolin-4-ones. Intrazeolite photoinduced rearrangements have also been investigated evidencing the directing role of the constrained reaction medium. Recent achievements include the preparation of fluoro-organically modified zeolites and their test as a new fluorinated constrained media for photooxidation reactions.

University of Pavia

The photochemistry group at Pavia (*Angelo Albini, Elisa Fasani, Maurizio Fagnoni*) has a long experience in organic photochemistry. A main field of research is the generation of highly reactive intermediates under the peculiar mild conditions of the photochemical experiment and their use in synthesis. A breakthrough has been the finding that phenyl cations virtually inaccessible by thermal methods are potentially useful synthetic intermediates generated under mild photochemical conditions by irradiation of electron-rich aryl chlorides and esters (mesylate, triflate and diethylphosphate). The photocleavage of the leaving group Y^- allows the formation of the phenyl cation ($ArY + h\nu \rightarrow Ar^+$). We are exploring the synthetic aspect of this intermediate and demonstrated the effective trapping by various π nucleophiles (alkenes, alkynes, aromatics) resulting in a smooth arylation procedure that rivals metal catalysis and is better performing from the environmental point of view. Another synthetic perspective we are exploring is photocatalysis for the mild selective activation of aliphatic C-H bonds in contrast to the harsh conditions required by thermal methods. In this way, the selective functionalization of C-H bonds (in alkanes, alcohols, aldehyde and amides) gives fine chemicals from largely available feedstock through a photocatalyzed hydrogen abstraction reaction.

A different field of active research is the photostability of drugs and sunscreens. As an example, various fluoroquinolone and oxazolidinone antibiotics are known to be phototoxic when exposed to UV light. The photochemistry is studied in various media in order to assess the mechanism operating in their photodegradation and may explain the photolability of drug preparations and the chemical basis of their toxic effect. Further family of drugs investigated are dihydropyridines, cardiac drugs and steroids. We also discovered that a significant loss of UV protection can be induced by the interactions between different solar UVB/UVA filters (a cinnamate and a benzoylmethane) simultaneously present in the same commercial suncreams.

Photodegradation of noxious substrates is also carried out, an example being the oxidation of sulfides by using molecular oxygen rather than expensive or more toxic oxidizing agents.

- Dondi, D.; Albini, A.; Serpone, N. Interactions between different solar UVB/UVA filters contained in commercial suncreams and consequent loss of UV protection *Photochem. Photobiol. Sci.* **2006, 5,** 835-843.
- Esposti, S.; Dondi, D.; Fagnoni, M.; Albini, A. Acylation of electrophilic olefins through decatungstate-photocatalyzed activation of aldehydes *Angew. Chem. Int. Ed.* **2007**, *46*, 2531-2534.
- Fagnoni, M.; Albini, A. Arylation reactions: the photo-S_N1 path via phenyl cation as an alternative to metal catalysis. *Acc. Chem. Res.* **2005**, *38*, 713-721.
- Fasani, E.; Albini, A.; Gemme, S. Mechanism of the photochemical degradation of amlodipine. *Int. J. Pharm.* **2008**, *352*, 197-201.
- Bonesi, S. M.; Carbonell, E.; Garcia, H.; Fagnoni, M.; Albini, A. Photocatalytic oxidation of aliphatic and aromatic sulfides in the presence of silica adsorbed or zeolite-encapsulated 2,4,6-triphenyl(thia)pyrylium *Appl. Catal. B-Environ.* **2008**, *79*, 368-375.

University of Perugia

Molecular Photophysics and Photochemistry

The research activity of this group at the Chemistry Department (section of Physical Chemistry) deals with the following topics:

- ***Photobehaviour of drugs*** (*F. Elisei, G. G. Aloisi, L. Latterini, A. Barbafina, B. Carlotti*) - The research project deals with a photophysical and photobiological study of organic compounds of pharmaceutical interest directed to understand the photosensitizing activity toward biological target molecules (membranes, proteins, DNA, polynucleotides). Information on the various decay pathways of the drug excited states and on transient species formed upon irradiation and the changes in the photophysical parameters (quantum yields and decay times) in the presence of bio-macromolecules allow to obtain information on the nature and mechanism of the interactions. Combining the photophysical results with the photobiological data, conclusions can be reached on the phototoxycity or phototerapeutic mechanism of the organic compounds.

The recent acquisition of fs-transient absorption and fluorescence up-conversion setups (time resolution ca. 130 fs in absorption and 80 fs in emission) allows gaining spectral and kinetic information on primary relaxation steps of excited states and on dynamic processes of simple and complex systems.

- Photobehaviour of arylolefins (*A. Spalletti, G. Bartocci, U. Mazzucato*) – This research line is focused on the luminescence properties, photoreaction (isomerization, cyclization) mechanisms and conformational equilibria of diarylethenes and distyrylarenes. The effects of heteroatoms, additives (energy, electron and proton donor/acceptors) and complex matrices are investigated. Particular attention is actually deserved to the study of systems where the excited compound photoisomerizes on a unique potential energy surface (adiabatically) giving directly the other excited isomer.

- **Chromogenic systems** (*G. Favaro, F. Ortica, P. L. Gentili, U. Mazzucato*) – The study deals with several interrelated lines: (i) spectral and kinetic behaviour of new photochromic compounds, belonging to the classes of spirooxazines and chromenes, that exhibit thermally reversible coloration, and to the class of bistable diarylethenes, that can be switched on-off by using light of different wavelength (UV and Visible); (ii) inclusion of photochromes into organised systems and solid matrices searching for a route to optically switchable smart materials for applications; (iii) role of selective electronic and vibronic excitation on the photochromic reaction for the photocontrol of photochemistry and fluorescence; (iv) interaction of photochromic compounds with biomolecules; (v) development of fuzzy logic systems based on the multiple outputs of the chromogenic compounds, and (vi) search for chromogenic compounds that, in one or both the interconverting molecular forms, exhibit fluorescence to be used as switching signal for readout systems.

- ***Nanostructured materials*** (*L. Latterini, G.G. Aloisi, F. Elisei*) – A structural, photophysical and photochemical study of complexes formed between inorganic matrices (layered double hydroxides, cloisites) and chromophores is carried out with the aim to prepare nano-hybrid materials with controlled photochemical behaviour. The investigation of material luminescence allows to reach a deeper knowledge on the constrained environment effects in the photophysical and photochemical behaviour of organic chromophores. More detailed information on non-homogeneous organic-inorganic hybrid materials are achieved by confocal fluorescence microscopy (lateral resolution ca. 250 nm).
This characterization has been recently extended to polymer nanocomposite materials where the inorganic matrices labelled with chromophores are used as fillers. The local chromophore fluorescence properties (intensity and spectra) give knowledge on the filler-polymer interfaces and on the filler distribution in the polymer.
With the aim to prepare optical sensors for biological systems, attention is devoted to the synthesis and characterization of organic and inorganic nanoparticles as sensitive and versatile building blocks of new functionalised materials. In particular, semiconductor and metal nanoparticles were synthesized directly in water in different experimental conditions in order to tune their optical properties. The capacity of the nanoparticles to interact with biological macromolecules (amino acids, proteins, phospholipidic membranes, cells) has been proved by bulk and space resolved fluorimetric techniques.
Organic nanoparticles are prepared to optimize this approach for transferring hydrophobic molecules in aqueous media to be used in the drug-delivery.

- ***Studies in the field of cultural heritage*** (*A. Romani, G. Favaro*) – Application of photochemical techniques in the field of cultural heritage is mainly devoted (i) to the study of degradation of materials (especially organic dyes) constituting works of art due to exposure to light (photoageing) and (ii) to recognition of original and restoration materials on polychrome surfaces by recording absorption and fluorescence reflectance spectra. For direct investigations on original artifacts, easily portable instrumentation (for absorption, colorimetry and steady state/time resolved fluorescence measurements) have been developed for *in situ* non-destructive investigations.

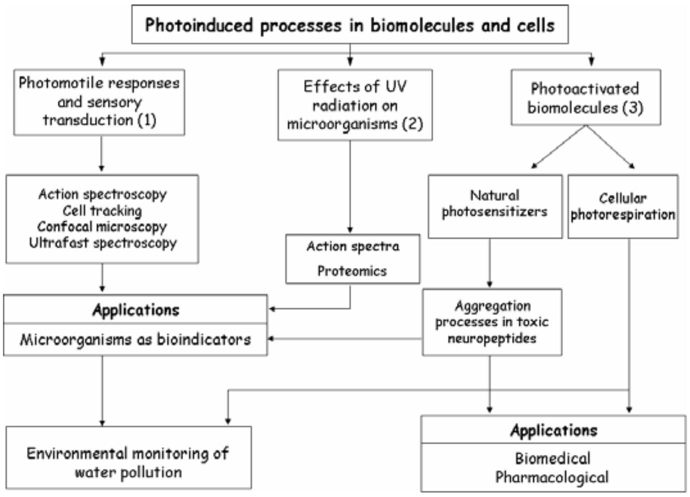
- ***Liquid scintillators*** (*F. Masetti, F. Ortica, A. Romani*) – The optical properties of mixtures of liquid scintillators are investigated (in collaboration with physical groups) with the aim of optimizing their emission yield, response time, attenuation length and durability in view of their use in large-scale detectors of solar neutrinos.

Photocatalysis

Another group is operative in Perugia in the framework of a collaboration between the "Dipartimento di Chimica" (Organic Chemistry Section: C. Rol and T. Del Giacco) and the "Dipartimento di Ingegneria Civile ed Ambientale" (M. V. Sebastiani) in the field of photocatalysis and green chemistry. This group is particularly concerned with photosensitized oxidations in homogeneous and heterogeneous phase. The reactions sensitized by semiconductors, as TiO_2 in heterogeneous phase, are actual technologies to decontaminate aqueous wastes and gaseous effluents.
The research work includes the following aspects: 1) a basic study on the mechanism of sensitized photo-oxidations in homogeneous phase of some benzylic derivatives; 2) mechanistic investigation of TiO_2 (commercial powder) sensitized photo-oxidation in aqueous phase of the same substrates; 3) realization of a photoelectrochemical technology to decontaminate waste water through TiO_2/Ti photoanodes; 4) preparation of nanostructured TiO_2 powders and determination of their photocatalytic efficiency; 5) evaluation of the photocatalytic efficiency of semiconductor films on various supports (metallic, polymeric, ceramic and vetrous materials) for atmospheric decontamination, 6) study of the degradation mechanism of suitable gaseous organic compounds with simple structure.

CNR Institute of Biophysics, Pisa

The main research activity of the "Photoprocesses in biomolecules and cells" Group [Staff: G. Checcucci, G. Cercignani (UNI PI), G. Colombetti, F. Ghetti, D. Gioffrè, F. Lenci, S. Lucia, R. Marangoni (UNI PI), A. Pietrangeli, A. Sgarbossa] can be thus schematised:



(1) The main objective of this research line is understanding the molecular basis of photoreception and photosensory transduction in aneural microorganisms. Several experimental approach are used such as optical spectroscopies in *in vitro* systems, confocal microscopy on intact cells, computer-assisted cell tracking.

Sgarbossa, A., G. Checcucci and F. Lenci (2002) "Photoreception and photomovements of microorganisms" *Photochem. Photobiol. Sciences*, 1, 459; S. Lucia, G. Cercignani, A. Frediani and D. Petracchi (2003) "Color-specific conditioning effects due to both orange and blue stimuli are observed in a *Halobacterium salinarum* strain devoid of putative methylatable sites on Htrl" *Photochem. Photobiol.* 77, 110; P. Plaza, M. Mahet, Monique M. Martin, G. Checcucci and F. Lenci (2007) "Target analysis of primary processes involved in the Oxyblepharismin-Binding Protein" *J. Phys. Chem. B*, 111, 690; Marangoni R., Lucia S. and G. Colombetti (2003), "Photomovements in Ciliates" in CRC Handbook of Organic Photochemistry and Photobiology, 122-1, Horspool W and Lenci F., eds., CRC Press; G. Colombetti, G. Checcucci, S. Lucia, C. Usai, P. Ramoino, P. Bianchini, M. Pesce, G. Vicidomini and A. Diaspro (2007) "Evidence for Ciliary Pigment Localization in Colored Ciliates and Implications for Their Photosensory Transduction Chain:A Confocal Microscopy Study" *Microscopy Research and Technique*, 70, 1028

(2) This line is aimed at characterizing the UV adverse effects on aquatic microorganisms and identifying molecular markers (proteins and/or genes) which can be used to obtain a quantitative measure of the UV-induced stress degree in real ecosystems. The investigation is focused both on molecular studies on single species and on self-sustaining microecosystems.

F. Ghetti, H. Herrmann, D.-P. Häder and H.K. Seidlitz, (1999) "Spectral dependence of the inhibition of photosynthesis under simulated global radiation in the unicellular green alga *Dunaliella salina*" *J. Photochem. Photobiol.* 48, 166; F. Ghetti, C. Bagnoli (2004) "Environmental Action Spectroscopy" in CRC Handbook of Organic Photochemistry and Photobiology, 114-1, Horspool W and Lenci F., eds., CRC Press; R. Marangoni, N. Messina, D. Gioffré and G. Colombetti (2004), "Effects of UV-B Irradiation on a Marine Microecosystem" *Photochem. Photobiol.*,80, 78; R. Marangoni, F. Marroni, D. Gioffré, F. Ghetti and G. Colombetti (2004) Biological Weighting Function of the UV-B induced impairment of phototaxis in the fresh water ciliate *Ophryoglena flava*, *Photochem. Photobiol.* 80, 408; L.Fulgentini, R. Marangoni and G. Colombetti (2008) "Optimizing soluble protein extraction and 2D-PAGE quality for extremophile ciliates" *Electrophoresis,* in print

(3) In this reserch line, the photophysical and photochemical properties of natural pigments, like hypericin and blepharismins, are investigated as photodynamic chromophores as well as inhibitors of the neurotoxic aggregation of peptides. In addition, the mitochondrial enzyme Cytochrome *c* oxidase (CcOX), is studied as possible photoacceptor in the visible-light-induced increase of O_2-consumption rate in living cells of different taxa.

Sgarbossa, A., T. Youssef and F. Lenci (2003) "Photosensitized structural modifications of the lens protein α-crystallin: do all modifications impair chaperone-like activity?" *Photochem. Photobiol.* 77, 567; A. Sgarbossa, F. Lenci (2008) "Aromatic interactions among β-amyloid peptides and small polycyclic molecules: possible mechanisms of fibrillogenesis inhibition" *Biophysical Inquiry into Protein Aggregation and Amyloid Diseases*, P.L. San Biagio and D. Bulone, Eds., Transworld Research Network, Kerala, India, in press; A. Remedi, L. di Salvo, G. Cercignani, S. Lucia, G. Colombetti (2007) "The effect of visible light irradiation on the oxygen consumption rate by cultured cells of different taxa." *Europ. Biophys. J. 36. S226*

Universities of Roma

The research groups of Enrico Baciocchi and Osvaldo Lanzalunga at the **University of Roma Sapienza** (Dipartimento di Chimica) and Massimo Bietti at the **University of Roma Tor Vergata** (Dipartimento di Scienze e Tecnologie Chimiche), are currently investigating several aspects of the properties and reactivities of oxygen centered radicals.

Nanosecond laser flash photolysis and steady-state photolysis are employed to study a variety of uni- and bimolecular processes involving alkoxyl, peroxyl and *N*-oxyl radicals. The processes under investigation include: (i) fragmentation and rearrangement reactions; (ii) hydrogen transfer reactions from C−H, N−H and O−H bonds of selected substrates; (iii) addition reactions to olefins and phosphorus derivatives; (iv) electron transfer (ET) reactions with electron rich compounds. Attention is devoted to the comprehension of the role of structural and medium effects on the alternative reactive pathways of these intermediates. Recent examples dealt with the mechanistic investigation of the *O*-neophyl rearrangement of 1,1-diarylalkoxyl radicals, the ET and hydrogen atom transfer reactivity of the phthalimide *N*-oxyl radical (PINO) in its reactions with ferrocenes, phenols and *N*,*N*-dimethylanilines.

At the University of **Roma Tor Vergata** another group is active in the field of photochemistry at the Department of Chemical Sciences and Technologies (Laboratory of Spectroscopy of Biological

Molecules, principal Investigators: Basilio Pispisa, Lorenzo Stella, Mariano Venanzi).

Actual Research Interest:
- Optical Spectroscopy of Biomolecules;
- Characterization of excited state processes in conformationally-constrained peptides functionalized with energy- or electron transfer donor-acceptor groups;
- Photocurrent generation through peptide self-assembled monolayers supported on gold and ITO electrodes;
- Application of fluorescence spectroscopy methods to investigate the mechanism of peptide insertion and membrane permeabilization by antimicrobial and cell penetrating peptides;
- Application of optical microscopy and scanning microscopy to the characterization of biomaterials (peptide self-assembled monolayer, liposome formulations, micelles).

Recent Publications:
'Electroconductive and photocurrent generation properties of self-assembled monolayers formed by functionalized, conformationally-constrained peptides on gold electrodes'
J.Pept.Sci. (2008) 14, 184-191
'Alamethicin Interaction with Lipid Membranes: A Spectroscopic Study on Synthetic Analogues'
Chemistry&Biodiversity (2007) 4, 1299-1312
'Peptide folding dynamics: a time-resolved study from the nanosecond to the microsecond time regime'
J.Phys. Chem. B (2006) 110, 22834-22841
'Effect of peptide lipidation on membrane perturbing activity: a comparative study on two trichogin analogues'
J. Phys. Chem.B (2006) 110, 22813-22818.

Laboratory for Computational Photochemistry and Photobiology

Dipartimento di Chimica, Università di Siena, Italy.
Chemistry Department, Bowling Green State University, OH, USA

The Laboratory for Computational Photochemistry and Photobiology (**LCPP**) (Head: Massimo Olivucci) is a bi-national lab devoted to the development of tools for mapping excited state potential energy surfaces and for the systematic characterization of the photochemical reactivity of different classes of organic and biological chromophores.

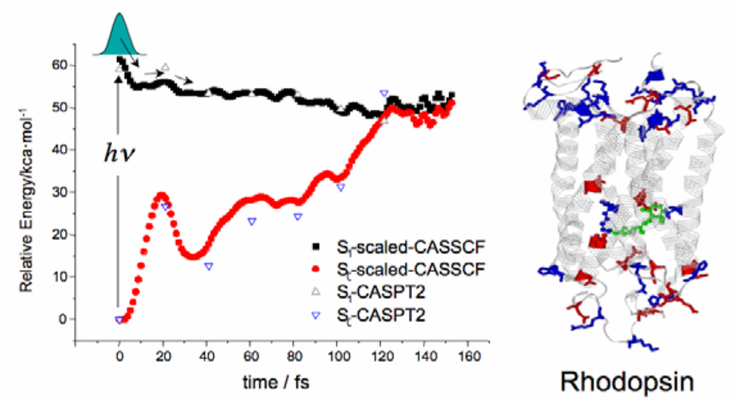
1. Background

The main target of LCPP is to help to establish and consolidate a branch of computational chemistry *entirely devoted to the investigation of light-induced phenomena* in molecular and bio-molecular materials. This also includes the introduction of new generations of MSc and Graduate students to the methods of theoretical and computational photochemistry. The research activity focuses on the development and application of state-of-the-art computational protocols for the simulation of photophysical and photochemical processes in both isolated chromophores and in the condensed phase. Ultimately, these methodologies will be used to provide an atomic-level description of the mechanism of light energy transduction from the single-molecule level to complex systems.

The basic activity is dominated by the search for the mechanisms that control the light energy wastage and exploitation at the molecular level. It is expected that different technological applications, in the field of the control of the three-dimensional architecture and reactivity of molecules of technological or biological interest is pursued. This includes the design of molecular devices or biological molecules (i.e. peptides or proteins) with certain desired optical or photochemical properties. The development of *novel* (or more effective) computational tools is also part of our research activity. Further information on LCPP and activities can be found in the group homepage: http://ccmaol1.chim.unisi.it/).

2. Current Activity

Current research at LCPP is centered on the idea that the most efficient and yet tunable photochemical systems known in nature are biological photoreceptors (i.e. visual and sensory pigments and ion-pumps). For this reason two parallel research lines are pursued. The first line focuses on the investigation of the molecular mechanism



making a photoreceptor (a protein) or its mutants (1-2) efficient in terms of color tuning (both in absorption and emission), reaction selectivity, time scale and quantum yield. The second and parallel research line uses the same computational tools to design novel synthetic molecules that mimic the behavior of biological photoreceptors and can be employed as bio-mimetic molecular devices (3). For instance, one of the **LCPP** targets is the development of a library of photo-responsive unnatural amino-acids to be employed in biological or medical research. Due to its research and the need for efficient computer programs and hardware, **LCPP** constitutes a potential environment for interdisciplinary work involving the Computer Sciences, Biology and Chemistry including organic synthesis (4).

To pursue the above targets, **LCPP** uses innovative computational protocols. These protocols, whose efficiency in treating large molecular systems has been demonstrated (see the excited state time evolution computed for the visual pigment of superior animals Rhodpsin. Scheme above), aim to the simulation of the *behavior of an entire population of photo-excited molecules* (2) thus overcoming the limitations of ordinary single molecule simulations. While, presently, this represents a brute-force computational effort, such development is foreseen to dominate the computer aided design of photoresponsive material in the near future. We believe that this is apparent when considering that: (i) the majority of the technological application of photo-responsive materials involve the coherent (laser) or incoherent light irradiation of an entire sample and (ii) the availability of larger and larger arrays of fast processors (i.e. of computer clusters) will enable the simultaneous modeling of a statistically meaningful number of excited state molecules and, in turn, of an excited state population.

3. Equipment and Structure of the Laboratory

LCPP is a bi-national Lab which exploits the computer facilities both at the Department of Chemistry, University of Siena (UNISI), Italy and at the Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University (BGSU), Ohio. The laboratory, equipped with a pool of Lynux-based servers including a 26 nodes – 134 cores High Performance Computer Cluster based on Intel Xeon (Woodcrest and Clovertown) CPUs and installed at the BGSU campus. The currently most advanced software tool used in the laboratory is a quantum-mechanics/molecular-mechanics software based on multiconfigurational quantum chemistry. This facilities allow for the construction of realistic (i.e. quantitative) computer models of photo-excited chemical and biological systems. Most important LCPP aims at the creation of specific tools capable to track the time-evolution of the system making the lab activity highly complementary to that of the Ohio Laboratory of Kinetic and Spectrometry to which the LCPP has access. A larger number of processors and an improved software performance are being pursued to allow for a routinely affordable simulation time of excited state molecular population dynamics.

4. Selected publications that document the current research activity:

1. Braña, P., Strambi, A., Ferré, N. and Olivucci, M. The Color of Rhodopsins at the ab initio Multiconfigurational Perturbation Theory Resolution *Proc. Nat. Acad. Sci. USA* **2006**, 103, 17154-17159.

2. Frutos, L.-M., Andruniów, T., Santoro, F., Ferré N. and Olivucci, M. Tracking the Excited State Time Evolution of the Visual Pigment

with Multiconfigurational Quantum Chemistry *Proc. Nat. Acad. Sci.* **2007**, 104, 7764-7769.

3. Lumento, F. Zanirato, V., Fusi, S., Busi, E., Latterini, L., Elisei, F., Sinicropi, A., Andruniów, T., Ferré, N. Basosi, R. and Olivucci, M. Quantum Chemical Modeling and Preparation of a Biomimetic Photochemical Switch *Ang. Chem. Int. Ed.* **2007**, 119, 418-424.

4. Synthesis of bio-mimetic light-driven molecular switches via a cyclopropyl ring-opening/nitrilium ion ring-closing tandem reaction Vinicio Zanirato, Gian Piero Pollini, Carmela De Risi, Filippo Valente, Alfonso Melloni, Stefania Fusi, Jacopo Barbetti, Massimo Olivucci *Tetrahedron* **2007** 63, 4975-4982.

NETWORKS

UK Semiconductor Photochemistry Network

The EPSRC has recently funded the creation of a UK network of academics and industrialists working in the area of semiconductor photochemistry;
http://www.ukphotocatalystnetwork.org.uk/site_map.
The Network embraces all aspects of semiconductor photochemistry (SPC); most notably: photocatalysis, fine chemical, photo-assisted synthesis and solar energy conversion. Its aim is to encourage and support exploitation of the significant science base in the subject **within the UK** by bringing together the associated wide and expanding multi-disciplinary community of academics and industrialists.

The Network will:

- provide a forum for the free flow exchange and pooling of ideas, knowledge and techniques (through biannual meetings, visits, invited lectures and website networking)
- encourage interdisciplinary collaboration and the creation of advanced and innovative science, leading to improved quality and effectiveness of research bids in the subject (through highly focused task groups),
- promote commercial exploitation of the developed technologies (through technical workshops and industrial visits),
- improve and broaden the training of research workers/postgraduate students (through lab visits/stays, meetings and a dedicated postgraduate conference),
- highlight and promote the international science and technology position of UK research in semiconductor photochemistry (through a dedicated Network website, publications, conferences and a UK-based, dedicated international conference)

- facilitate collaboration and funding at a European level (through EU networks, such as COST, and FP7 funded research programmes).

Professor Andrew Mills
James Young Chair in Chemistry
Department of Pure & Applied Chemistry
University of Strathclyde

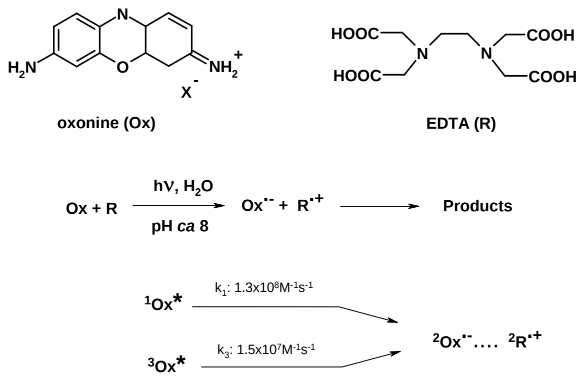
PERSONAL NEWS

Roland Bonneau : A Pure Photochemist

Born in 1942 near La Rochelle in Charente Maritime, a region of cognac and roman style churches, Roland Bonneau graduated in chemistry at the University of Bordeaux in 1964 and obtained a "Thèse d'Etat" (equivalent to-day to Ph.D.+ Habilitation) in 1971, entitled : "*Application de la spectroscopie par éclairs à l'étude des propriétés physicochimiques des états excités des colorants thiaziniques et de quelques hydrocarbures aromatiques*" under the supervision of professor J. Joussot-Dubien.

He was recruited as a CNRS researcher (attaché de recherches) in 1966, and became "maître de recherches" in 1979 (nowadays called "directeur de recherches", a term that he appreciates much less than "maître").

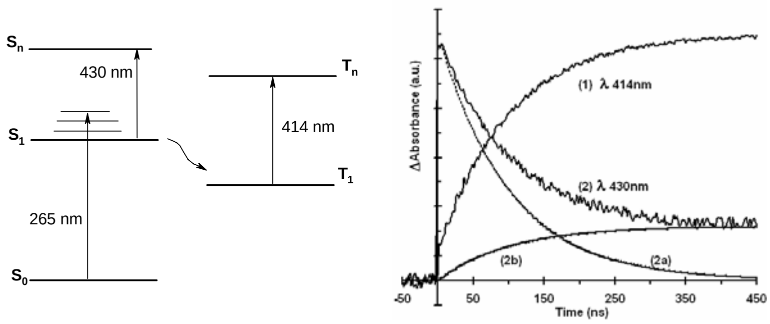
From the very beginning, Roland was immediately caught in the creative and enthusiastic atmosphere of the young laboratory of J. Joussot-Dubien. He began by investigating the photochemistry of thiazinic dyes under the guidance of Jean Faure. This work focussed on the determination, by flash photolysis, of triplet pK_A's and of the mechanism of photoinduced electron transfer. Some of these remarkable results are highlighted below, for example one of the first kinetic data on excited singlet *vs* triplet reactivity in the reduction of a dye (oxonine) by EDTA (1). It was shown (scheme 1) that the S_1 state is about an order of magnitude more reactive than the T_1 state, even if the quantum yields of effective electron abstraction are in the reverse order because the lifetime of S_1 is much shorter than that of T_1. Roland also investigated the influence of pH on the singlet oxygen production in aqueous solution, using thiazine dyes as sensitizers (2).



Scheme 1

In 1968, these investigations were interrupted by an unexpected event (not linked with the famous 1968 student unrest!), which opened new vistas in flash photolysis: The CGE company in Marcoussis (near Paris) had just set up a Neodynium laser providing 30 ns pulses at 265 nm, and wanted to test its performance. They contacted J. Joussot-Dubien, who responded immediately by dispatching Roland Bonneau and J. Faure in a car loaded with compounds and equipment. Together, they drove to Marcoussis and, after receiving technical advice from Lars Linquist, Roland set up one of the first laser flash photolysis instruments. He then examined naphthalene solutions because the T_1-T_n absorption of naphthalene was known. In addition to this expected transient, he discovered a second, unexpected, transient absorption that he assigned to the S_1-S_n transition (scheme 2). This was one of the very first observations in the singlet manifold (3). This pioneering work was followed by the investigation of other aromatic hydrocarbons by the new laser flash photolysis technique (LFP).

Then Roland, owing to his expertise in LFP, became deeply involved in the passionate problem of *double bond twisting*. At about that time, Lionel Salem concluded from calculations on the excited state of unsymmetrical alkenes that the π bond, twisted at 90°, should experience a sudden polarization generating a zwitterionic state which should be considerably stabilized by polar solvents such acetonitrile.

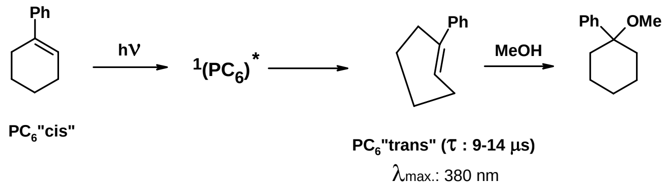


Energy diagram for naphthalene in methanol (10^{-4}M) at RT

LFP transients analysis
1) at 414 nm : T_1-T_n absorption
2) at 430 nm: S_1-S_n & T_1-T_n absorptions
2a) decay of S_1; 2b) growth of T_1

Scheme 2

Salem solicited Joussot-Dubien's group to test these theoretical results (theory ahead of experiment!). Roland selected *1-phenylcyclohexene* (PC6) whose absorption was appropriate for the laser light and in which twisting was impaired. He detected a transient (X) whose lifetime was found not to be sensitive to the solvent polarity ($\tau \approx 10$ µs in cyclohexane as in acetonitrile). This result ruled out the Salem zwitterion; the transient could not be a triplet state either, since its lifetime was unsensitive to oxygen. X was finally identified as the *trans* PC6 isomer in which the double bond of cyclohexene is twisted by more than 90°. This intermediate, postulated by Kropp to explain the photo-Markovnikov addition of methanol to PC6, was expected to be very unstable at ambient temperature and the reality of its existence was largely questioned at the time (4, most cited). The *trans* structure was later substantiated by X-ray spectroscopy of the Diels-Alder adduct of *trans* PC6 to *cis* PC6 in excess (5).



Scheme 3

The *trans*-1-phenylcycloheptene was detected and characterized shortly after in a similar fashion (6); owing to a lesser strain of the double bond, the absorption spectrum is shifted to higher energy and the lifetime is much longer (fig.1). To extend these novel observations to other double bonds, Roland turned to α-*enones*, whose spectra are ideally suited for the 353 nm laser light.

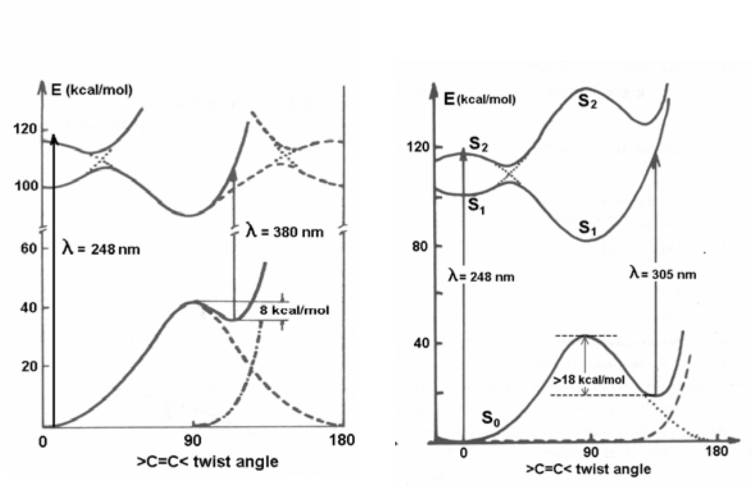
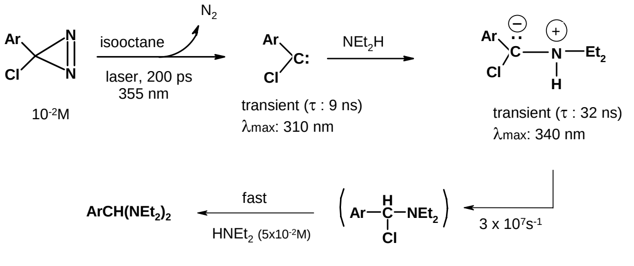


Figure 1: Energy profile for the photoisomerization of 1-phenylcyclohexene (left) and 1-phenylcycloheptene (right*)*

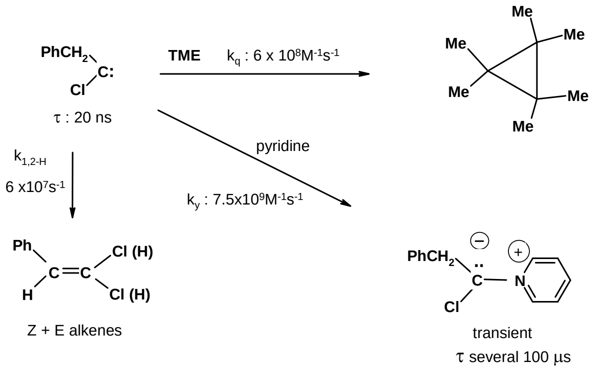
While the preceding isomerizations were due to excited singlet states, the introduction of a keto group favored intersystem crossing toward triplet states. Thus, for 1-acetylcyclohexene two transients appeared, identified respectively to a perpendicular triplet (λ max 280 nm, $\tau \approx$ 16 ns) not quenched by piperylene and to the *trans* isomer (λ_{max} 345 nm, τ = 15 µs in cyclohexane and acetonitrile); the formation of the *trans* species was shown to match kinetically the disappearance of the triplet state (7). Then, from a comprehensive analysis of the study of cyclohexenone, cycloheptenone and cyclopentenone, Roland assigned the transients absorbing at 260-280 nm to twisted triplets states (τ = 10-400 ns, depending on the angle of twist), giving for the first time a clear picture of the so-called phantom triplets (8). Moreover, Roland identified perpendicular triplets as intermediates in the *cis-trans* photoisomerization of styrenes (9). Regarding styrenes, their intersystem crossing quantum yield was believed to be extremely low because they fail to sensitize the phosphorescence of biacetyl. Roland obtained experimental evidence disproving this common idea. He found, for instance, $\phi_{isc} = 0.4$ for styrene (10)!

The successful involvement of Roland in the study of photochemical reaction mechanisms became so well known that many colleagues approached him from all around the world. Among them, his longstanding collaboration with Professor Michael Liu (Prince Edward Island, Canada), a specialist of diazirines and carbenes, is noteworthy. Carbenes were characterized in the 1950s and rapidly were shown to play a major role as intermediates in organic synthesis (cycloadditions, rearrangements ...). In particular, they can be generated by thermolysis and photolysis of diazirines (11). Although thermolysis usually works well to produce carbenes for synthetic applications, it may be desirable to use photolysis which can operate at lower temperatures and, most important for Roland, photolysis by (laser)-flashes allows one to determine the spectroscopic and kinetic properties of transient species, and thus reaction mechanisms (scheme 4).



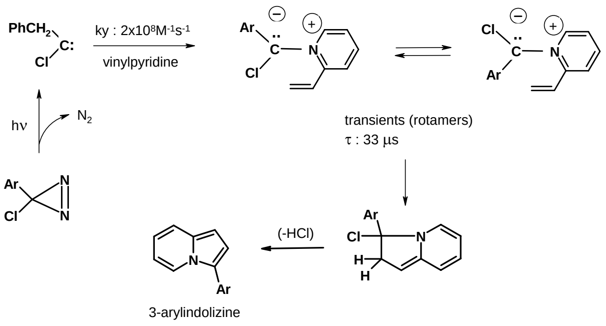
Scheme 4

One common but undesirable reaction observed in alkyl and benzylcarbenes is their rearrangement to alkenes or styrenes by 1,2-H shift. Roland contributed several papers (12, 13, 14) on the competition between rearrangement and addition of benzylchlorocarbenes (scheme 5). In addition, a complete kinetic study of alkylchlorocarbenes was conducted using LFP, thermolysis and time-resolved photoacoustic calorimetry (15).



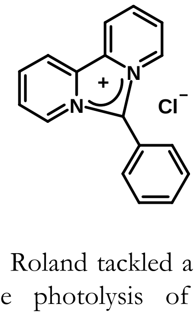
Scheme 5

Evidence of ylid formation from arylchlorocarbenes with aliphatic amines demonstrated a two-step mechanism (scheme 4) for the carbene insertion into the N-H bond (16). Bonneau and Liu then developed new synthetic reactions, with analysis of their mechanism, based on the formation of intermediate ylid species whose rearrangement gives the final products. They thus synthesized diverse heterocycles as illustrated (scheme 6) by the preparation of 3-substituted indolizines from 2-vinylpyridine ylids (17, 18). Several transients were characterized (carbene and two rotamers of the ylid) and the reaction rates and activation parameters were determined. Along the same lines, the one-step synthesis of 1,2,3-trisubstituted pyrroles at 25° C was described (19).



Scheme 6

In recent work, Roland isolated a diazatricyclic cationic compound (PDI), obtained as a result of the phenylchlorocarbene reaction upon 2,2'-bipyridine. Following this result, PDI could be prepared in a few hours by a one-step thermolysis in gram quantities in 90 % yield. Previously, PDI had been obtained after a month long process in 45 % yield. This is an example of photochemistry leading to an improvement of classical organic chemistry (20).



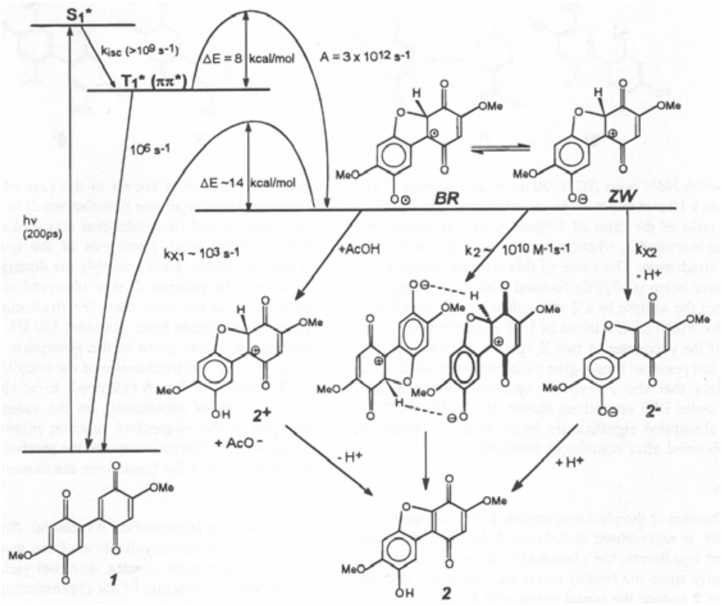
Phenyldipyridoimidazolium chloride

PDI

Roland tackled a number of other mechanistic problems,such as the photolysis of metalhexacarbonyl compounds (21), the characterization of new iodine aggregates in water (22), the determination of intersystem quantum yields (23), the photoprotonation of an arylsilane (24), the intramolecular cyclization of 2-vinylbiphenyl where, *inter alia*, he demonstrated with S. Lazare and R. Lapouyade that it is an adiabatic reaction in the triplet state (25). He was also successfully involved in the elucidation of the mechanism of phenylquinone cyclization (26, 27) and the photochemistry of a lignin-like quinoid dimer (28), with A. Castellan (scheme 7).

The statement by C. E. Guye that **"The scale of observation creates the phenomenon"** applies well to Roland Bonneau who essentially explored the nanosecond-microsecond time range where many photochemical events occur. Like a smart detective, he hunts down the suitable transients, follow them up and discard the false tracks. Roland has published more than one hundred papers, eighty per cent of which are co-authored with foreign colleagues. This unusual feature attests to his international stature.

In addition to administrative duties in Bordeaux, Roland served as a member of the IUPAC photochemistry committee for many years (1986-1998), acting as secretary in 1994-1998. During that period, he co-authored two articles in *Pure Appl. Chem.* on the recommendations to determine "molar absorption of transient species in solution" (29, 30). It was for him a hectic time as he was also running the French Group of Chemistry (1985-1992). Among his accomplishments, the first Italian-French meeting is remembered as a full success. Last but not least, the students of the Bordeaux "School of chemical Sciences" were privileged to have him as an excellent teacher in photochemistry.



Scheme 7

Roland Bonneau will be greatly longed in our laboratories, not only for his scientific knowledge, but also for his friendship, kindness and willingness to cooperate and give perceptive and precious advice. He will now have time for non-professional activities. We wish him an active and joyful retirement in the company of his wife Barbara and his children and grandchildren.

References

1 R. Bonneau *Photochem. Photobiol.,* **25** (1977) 129

2 R. Bonneau, R. Pottier, O. Bagno, J. Joussot-Dubien *Photochem. Photobiol.,* **21** (1975) 159

3 R. Bonneau, J. Faure, J. Joussot-Dubien *Chem Phys. Letters,* **2** (1968) 65

4 R. Bonneau, L. Salem, J. Joussot-Dubien, A.J. Yarwood *J. Am. Chem. Soc.,* **98** (1976) 4329

5 W.G. Dauben, H.C. van Riel, C. Hauw, F. Leroy, J. Joussot-Dubien, R. Bonneau *J. Am. Chem. Soc.,* **101** (1979) 1901

6 R. Bonneau, J. Joussot-Dubien, J. Yarwood, J.Pereyre *Tetrahedron Letters*, (1977) 235-238

7 R. Bonneau, Ph. Fornier de Violet *C.R. Acad. Sc. Paris,* **284** (1977) 632

8 R. Bonneau *J. Am. Chem. Soc.,* **102** (1980) 3816-3822

9 R. Bonneau *Journal of Photochemistry*, **10** (1979) 439-449

10 R. Bonneau *J. Am. Chem. Soc.,* **104** (1982) 2921-2923

11 R. Bonneau, M.T.H. Liu *J. Phys. Chem. (A),* **104** (2000) 4115-4120

12 M.T.H.Liu et R.Bonneau *J. Am. Chem. Soc.*, **111** (1989) 6873-6874

13 J.E.Jackson, N.Soundararajan, W.White, M.T.H.Liu, R.Bonneau, M.S.Platz *J. Am. Chem. Soc.,* **111** (1989) 6874-6875

14 M.T.H.Liu, R.Bonneau *J. Am. Chem. Soc.*, **112** (1990) 3915-3919

15 R. Bonneau, M.T.H. Liu, K.C. Kim, J.L. Goodman *J. Am. Chem. Soc.,* **118** (1996) 3829-3837

16 R. Bonneau, M.T.H.Liu *J. Am. Chem .Soc.*, **113** (1991) 9872-9873

17 R. Bonneau, Y.N. Romashin, M.T.H. Liu, S.E. MacPherson *Chem. Comm.,* (1994) 509-510

18 M.T.H. Liu, Y.N. Romashin, R. Bonneau *Int. Journal of Chem. Kinetics*, **26** (1994) 1179-1184

19 Y.N. Romashin, M.T.H. Liu, R. Bonneau *Chem.Comm.*, (1999) 447-448

20 R. Bonneau, M.T.H. Liu *Eur. J. Org. Chem.*, **15** (2005) 1532-1540

21 J.M. Kelly, C. Long, R. Bonneau *J. Phys. Chem.,* **87** (1983) 3344-3349

22 Ph. Fornier de Violet, R. Bonneau, J. Joussot-Dubien *Chem. Phys. Letters,* **28** (1974) 569

23 T. Brotin, J.P. Desvergne, F. Fages, R. Utermöhlen, R. Bonneau, H. Bouas-Laurent *Photochemistry and Photobiology* , **55** (1992) 349-358

24 J.P. Desvergne, R. Bonneau, G. Dörr, H. Bouas-Laurent *Photochem. Photobiol. Sciences,* **2** (2003) 289-296

25 S. Lazare, R. Lapouyade, R. Bonneau *J. Am. Chem. Soc.,* **107** (1985) 6604-6609

26 R. Bonneau, H. Moufid, G. Guyot *New J. Chem.,* **15** (1991) 257-265

27 S. Bearnais-Barbry, R. Bonneau, A. Castellan *Photochem. Photobiol.,* **74** (2001) 542-548

28 S. Bearnais-Barbry, R. Bonneau, A. Castellan *J. Phys. Chem. (A),* **103** (1999) 11136-11144

29 R. Bonneau, I. Carmichael, G.L. Hug *Pure & Applied Chemistry,* **63** (1991) 289-299

30 R. Bonneau, J. Wirz, A. D. Zuberbühler *Pure & Appl. Chem.*, **69** (1997) 979-992

Henri Bouas-Laurent, Jean-Pierre Desvergne and Dario Bassani
Institut des Sciences Moléculaires
Université Bordeaux 1, Talence, France

TECHNICAL REPORT

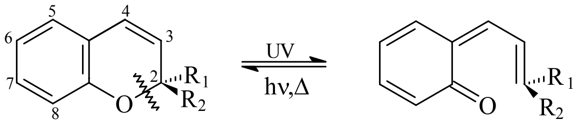
The Effect of the Electronic State, Vibrational Mode and Level Excited on Photochemistry and Photophysics

Ralph S. Becker *§ and Gianna Favaro#

§ ralphbecker25@sbcglobal.net
#Università di Perugia, Dipartimento di Chimica, 06123 Perugia, Italy

This review will not go into any experimental details. The references given can be consulted for information. The review will describe new concepts, models, mechanisms and appropriate equations previously not considered in the fields of photochemistry (PC) and photophysics (PP). These are generally in sharp contrast to what has been classical believed.

The first hint of a potentially unique find came in 1966 when we noticed that the fluorescence (F) excitation spectrum of a photoactive chromene, was significantly different from the absorption spectrum.[1] In this work, we showed that photochromic behavior was present with substitution at any position or with benzo condensation as long as the chromene (or pyran) unit was present, see scheme 1. Some qualitative ideas for the behavior were given. Proof of the nature of the product was also determined.[2]



Scheme 1

In 1969[3] a much expanded and quantitative explanation was made of the phenomenon seen earlier. Here, the relative quantum yields of F,

Φ_F^{rel}, were determined for all the vibronic levels in all of the excited states for a chromene and benzochromene. It was found that Φ_F^{rel} markedly varied, up to 10-fold, as a function of the electronic state, the vibrational mode and level that was excited. Comparison was made to a molecule of similar structure to 2,2-diethylchromene except the O atom was replaced by $-CH_2$ (1,2-dihydronaphthalene). The latter did *not* show photochemistry (PC) over irradiation times comparable to the chromenes. In this case, excitation over fifteen wavelengths between 296 nm and 250 nm (first entire transition) did not result in any deviation (± 5%) of Φ_F^{rel}.

A mechanism and associated equations were developed to understand the strong dependence of Φ_F^{rel} on the particular vibronic level excited for molecules that underwent PC. Also, we determined that no phosphorescence was present and in later works by us,[4, 5] no triplet transient was found for chromenes and benzochromenes except for a small amount for molecules having a 7,8-benzochromene core. Therefore, we considered that the PC was in competition with vibrational relaxation at every vibronic level. With this premise, the fraction of molecules that relax from an upper (n) to a lower (n-1) vibronic level within a given mode is:

$$k_v/\,(k_v + k_{PC}\,) \qquad (1)$$

where k_v is the vibrational relaxation constant (called k_{IC} in ref.3) and k_{PC} is the PC rate constant. For n such levels:

$$\Phi_F^{rel}(n)=[k_v/(k_F + k_{PC})]^n \qquad (2)$$

A plot of log Φ_F^{rel} vs. n should give a straight line with a slope equal to log $[k_v\,/(k_F + k_{PC})]$ and from this the ratio of $k_v/\,k_{PC}$ can be obtained. There was a wide variation in the ratio as a function of the state and mode (sequence was used in ref. 3) that was excited.

We also were able to show the foregoing phenomenon occurred in other types of photoactive compounds such as indolinospiropyrans and fulgides but with less resolution of the absorption spectrum.[6,7]

The one missing piece of experimental data to unequivocally establish the correctness of the model of 1969[2] was the evaluation of the Φ_{PC} as a function of n. The fact that the PC was involved was secure based on the results of photoactive systems as given above and the absence of the vibronic and state effects in a molecule with no PC.[3] In 1999 we experimentally determined both the *absolute* Φ_{PC} and Φ_F for a different photoactive chromene.[8] With the consideration of the non-radiative process from S_1 (not including intersystem crossing since it was not found in any molecule studied thus far), a somewhat modified equation resulted:

$$\Phi_F(n) = \Phi_F(0)\Phi_V^n \qquad (3)$$

where $\Phi_F(n)$ is the experimentally *absolute* quantum yield of F as a function of the vibronic level (n) and state that were excited and:

$$\Phi_F(0) = k_F/(k_F + \sum k_i) \qquad (4)$$

is the quantum yield of F from n = 0 of S_1 where $\sum k_i = (k_{PC} + k_{NR})$

$$\Phi_V = k_V/(k_V + k_{PC}) \qquad (5)$$

is the vibrational relaxation quantum yield, in the absence of triplet formation, and is a measure of the efficiency of relaxation from one vibronic level to another (in competition with PC) within a given mode and is assumed to be constant within a given mode, see figure 1. *Note that the concept of a vibrational relaxation quantum yield has never been considered before in the arenas of PC or photophysics (PP).* From a plot of the ln of eq. 3 as a function of n, the slope is related to Φ_V and the intercept to $\Phi_F(0)$. There is considerable dependence of the experimental F yield upon the vibronic and state levels excited.[8]
Furthermore, based on the new model in figure 1, a new equation, (6), was developed to evaluate $\Phi_{PC}(n)$ and its dependence on Φ_V and the vibronic or state level excited.

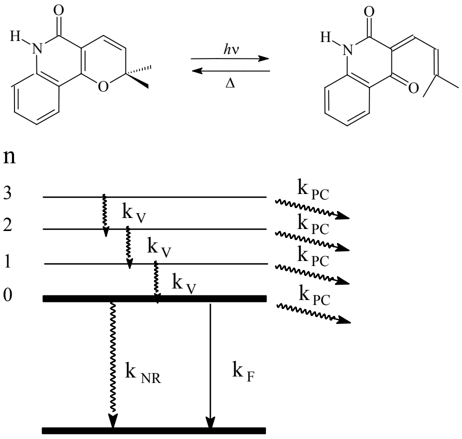


Figure 1. Model for the fate of quanta absorbed into any vibronic level of S_X (x=1 in figure) excluding intersystem crossing.

$$\Phi_{PC}(n)= \Phi_{PC}(0)\Phi_V^{n} + \Phi_{PC}\{1 + \Phi_V + \Phi_V^{2} + \ldots\ldots\ldots\ \Phi_V^{n-2} + \Phi_V^{n-1}\} \quad (6)$$

where

$$\Phi_{PC}(0)= k_{PC}/(k_{PC} + k_{NR}+ k_F) \quad (7)$$

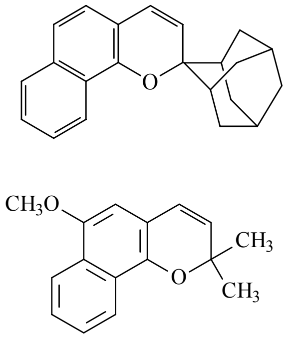
and

$$\Phi_{PC}=k_{PC}/(k_{PC} + k_V\,) \quad (8)$$

For example: for n=0, $\Phi_{PC}(0) = k_{PC}/(k_{PC} + k_{NR}+ k_F)$ and
for n=1. $\Phi_{PC}(1) = \Phi_{PC}(0)\ \Phi_V + \Phi_{PC}$ and
for n=2, $\Phi_{PC}(2) = \Phi_{PC}(0)\ \Phi_V^{2}+\Phi_{PC}(1+\Phi_V)$

Note again the introduction of a new term Φ_{PC} that is *not* the experimental yield of PC but measures the efficiency of PC from levels within a mode relative to that of vibrational relaxation to lower levels and is assumed to be constant within a given mode, see figures 1 and 2. *Note here, as for the case of Φ_V, that Φ_{PC} is a new concept for* *consideration in PC/PP processes.* The experimental PC yield, [$\Phi_{PC}(n)$], varied significantly as a function of the level excited (n). For example for n = 0, the yield was 0.4 whereas for n = 5, the yield was ~ 1.[8]

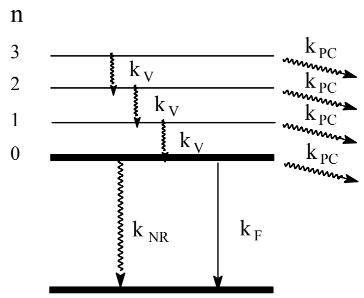
The yield of F was quite low but did show an inverse relationship to that of PC as would be expected from the model. We will now consider two molecules, scheme 2, that do not show F in fluid solution or in glasses at 80 K.[9]



AD LAP

Scheme 2

To help keep in mind the new model, applicable symbols and equations, fig. 2 offers a summary of all of these.



$$\Phi_F(n) = \Phi_F(0)\ [k_V/(k_V + k_{PC})]^n = \Phi_F(0)\ (\Phi_V)^n \qquad (3)$$

$$\Phi_V = k_V / (k_V + k_{PC}) \qquad (5)$$

$$\Phi_F(0) = k_F / (k_F + k_{PC} + k_{NR}) \qquad (4)$$

$$\Phi_{PC}(n) = \Phi_{PC}(0)\ \Phi_V^n + \Phi_{PC}(1 + \Phi_V + \Phi_V^2 + \ldots\ldots \Phi_V^{n-2} + \Phi_V^{n-1}) \qquad (6)$$

$$\Phi_{PC}(0) = k_{PC}/(k_{PC} + k_F + k_{NR}) \qquad (7)$$

$$\Phi_{PC} = k_{PC} / (k_{PC} + k_V) \qquad (8)$$

Figure 2. Summary of the model, symbols and equations developed.

Here we wished to obtain the effect of the electronic state as well as the vibrational mode and level excited on just the yields of PC at 80 K to further test the models previously proposed by us.[3,8] In addition, we wanted to explore the consequences of exciting into combination bands/levels.

There are two identifiable modes in the S_1 state of both AD and LAP of ~380 cm^{-1} and ~1380 cm^{-1}. In the S_2 state, the frequencies are similar, ~390 cm^{-1} and ~1360 cm^{-1}. Consider the low energy mode as v' and other mode as v. The experimental yield of PC[$\Phi_{PC}(n)$] increased when exciting from 0 into 1v' and further increased upon exciting into 2v' but then relatively decreased when exciting into v, table 1. If excitation was to the *0 level of S_2, the PC yield was lower than any and all levels of S_1* [except $S_1(0)$ of LAP], *a total of eight,* despite the fact that the S_2 state is 9,000-10,000 cm^{-1} (~26-29 kcal/mole) *greater* in energy. Also note that excitation into combination levels showed that the PC yields were greater than those of the fundamental mode upon which they were built, table 1 and fig. 3. The individual Φ_V and Φ_{PC} could be obtained for the two modes of the S_1 state.[9]

It is clear from the data that the PC yield is markedly sensitive to the vibronic level as well as the state that is excited, table 1. Also note the substantial increase in the PC yield with the addition of even one quantum of vibrational energy in both S_1 and S_2, table 1. We have previously seen the *inverse of the foregoing for F*.[3,8]

Others have seen evidence that "hot excited-state PC" occurred.[10,11] It was believed that the PC could compete with cooling of large molecules. However, the authors were not at all convinced that vibronic level discrimination was responsible. Rather, they believed an increase in the energy of excitation by itself was the reason for the increase in PC.

	vibrational analysis	Φ of LAP reaction	Φ of AD reaction
S_1	0	0.09	0.12
	0+ν'	0.58	0.69
	0+2ν'	0.86	0.95
	0+ν	0.58	0.72
	0+ν+ν'	0.73	0.79
	0+ν+2ν'	0.82	0.94
	0+2ν	0.77	0.84
	0+2ν+ν'	0.77	0.91
	0+2ν+2ν'	0.86	0.98
S_2	0	0.22	0.07
	0+ν	0.55	0.67

Table 1. PC yields for AD at 80 K as a function of the level excited above zero of S_1

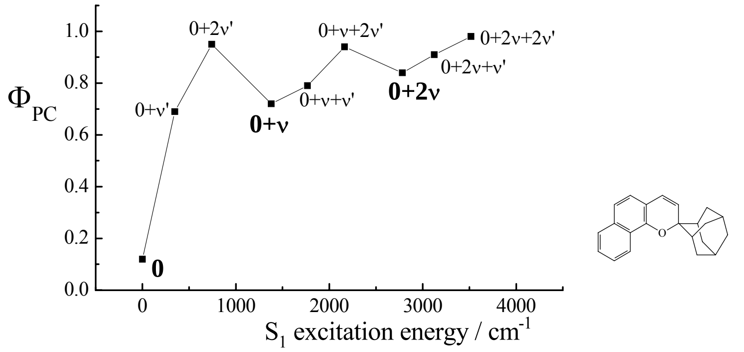


Figure 3. Trend in PC yields of AD as a function of excitation to levels above n = 0 of S_1

Our results discussed above and later unequivocally demonstrate that the experimental yields of PC can be dependent on the electronic state, the vibrational mode and the level that is excited. *The necessary condition is that PC be competitive with vibrational relaxation at any level (state or vibronic) that is excited*, figure 2. From this model, appropriate equations have been developed to predict $\Phi_F(0)$, $\Phi_F(n)$, $\Phi_{PC}(0)$ and $\Phi_{PC}(n)$, fig.2, and eqs. 3,4,6,7 utilizing the new concepts of quantum yields of vibrational relaxation Φ_V and photochemistry Φ_{PC} (fig 2 and eqs. 5 and 8). The fluorescence quantum yield in the presence of PC will also be dependent on the state and vibronic level excited if relaxation and PC are competitive at those levels.

In 2005[5] we examined two molecules having the same 2,2-dimethylchromene core but differed in the position of a benzo condensation, scheme 3.

5,6-DMBC

7,8-DMBC

Scheme 3

This resulted in the 5,6- derivative (5,6DMBC) showing both F (τ = 5 ps, fluid solution) and PC while the 7,8 derivative (7,8DMBC) did not show F ($\Phi \leq 10^{-5}$) but did show some triplet formation (τ = 0.84 ms, fluid solution) as well as PC. Tables 2 and 3 present the data for F and PC as a function of the state and vibronic level excited.

We can simplify the equation (6) for calculating the $\Phi_{PC}(n)$ if we express it as a sum of the PC yield of the level excited plus that level to which the molecule relaxes:

$$\Phi_{PC}(n) = \Phi_{PC} + \Phi_V \Phi_{PC}(n-1) \qquad (9)$$

From a plot of $\Phi_{PC}(n)$ vs. $\Phi_{PC}(n-1)$ the Φ_V is the slope and the Φ_{PC} is the intercept for any mode of any excited state. Thus there are two independent methods to obtain Φ_V: one from F, eq. 3, and the other from eq. 9.

Once again for both molecules we can see the strong dependence of the experimental yields of PC on the state and vibronic level that is excited, tables 2 and 3. Also, although the yield of F is small for 5,6DMBC, the yield of F shows a similar sensitivity through three electronic transitions. Note the significant difference of the dependence of the yield of F on the mode that is excited for both molecules. Also note the significant lower yield of PC for the 0 levels of all three states compared with those of any vibronic higher or lower in energy. *Photochemistry can occur from any level of any mode of any state. Thus there is large number of experimental yields of PC, $\Phi_{PC}(n)$. Fluorescence occurs only from $S_1(0)$ but the quantity/yield depends on the vibronic level excited (on the relative magnitudes of the competitive rate constants k_{PC} and k_V typical of each mode, see fig. 4).*

We also see, as earlier, that relaxation occurs only within the particular mode excited. *This means there is no crossing between different modes during relaxation*—we also saw this earlier for AD and LAP. Again we wish to emphasize that this observation/statement is in marked contrast to what has been believed photochemistry and photophysics.

For 7,8DMBC there is no relaxation path from $S_2(0)$ via vibronic levels of S_1 nor directly to $S_1(0)$. For 5,6DMBC, we cannot exclude the possibility that relaxation occurs from the 0 level of upper states to the 0 level of lower states. However, we can say that relaxation from $S_3(0)$ and/or $S_2(0)$ does not occur via fundamental, harmonic or combination levels of S_1 nor does relaxation from $S_3(0)$ occur via similar types of levels appropriate to S_2. Also note for this molecule that the yield of PC from excitation into $S_2(0)$ at ~ 37,000 cm^{-1} (table 1) is notably *smaller than from any level of lower energy* (up to 9,000-10,000 cm^{-1} (~27 kcal/mole). The rate constant for $k_{PC}[S_1(0)]$ is ~ 8000 fold greater at 80 K than for 5,6DMBC[5]. Table 4 presents all of the yields, rate constants, lifetimes for both molecules.

Wavelength	Energy	ΔE	Assignment	$\Phi_{PC}(n)$
359	27855	0	0	0.16±0.01
354	28250	395	0+360	0.42±0.02
350	28570	715	0+2 × 360	0.64±0.03
342	29240	1385	0+1360	0.39±0.02
338	29585	1730	0+1360+360	0.53±0.02
334	29940	2085	0+1360+2×360	0.70±0.03
330	30305	2450	0+1360+3×360	0.76±0.04
327	30580	2725	0+2 × 1360	0.58±0.03
323	30960	3105	0+2×1360+360	0.68±0.03
319	31335	3490	0+2×1360+2×360	0.74±0.04
314	31850	3990	0+3×1360	0.83±0.04
271	36900	0	0	0.10±0.01
268	37310	410	0+390	0.24±0.01
261	38310	1410	0+1400	0.31±0.02
258.5	38684	1785	0+1400+390	--
252	39680	2780	0+2×1400	--

Table 2. Assignment of vibrational modes and levels and accompanying photochemical yields at 80 K for 7,8 DMBC

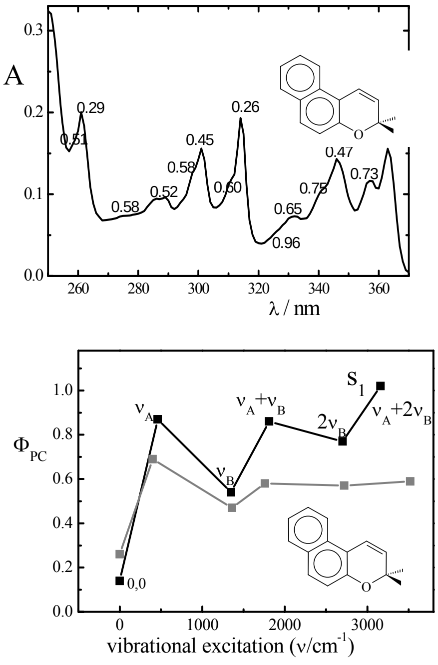


Figure 4 - Trend in PC yields of 5,6DMBC as a function of excitation to levels of S_1 and S_2

In particular note the large values for Φ_{NR} directly from S_2 and S_3 to the ground state S_0 for 7,8DMBC which is true for other benzochromenes not showing fluorescence.[9] Thus in general a direct non-radiative coupling/path can occur from an excited pure state $S_X(0)$ to the ground state S_0.

λ (nm)	E (cm^{-1})	ΔE (cm^{-1})	Assign.	$\Phi_{PC}(n)$	$\Phi_{F}(n)$
363.5	27510	0	0	0.14±0.01	0.033±0.01
357.5	27970	460	0+460	0.87±0.12	0.035±0.01
347	28820	1310	0+1350	0.54±0.05	0.026±0.007
341	29325	1815	0+1350+460	0.86±0.08	0.024±0.004
331	30210	2700	0+2×1350	0.77±0.10	0.023±0.005
326	30670	3160	0+2×1350+460	1.02±0.09	0.016±0.001
315	31750	0	0	0.26±0.02	0.012±0.001
311	32150	400	0+400	0.69±0.09	0.012±0.002
302	33112	1362	0+1360	0.47±0.06	0.0093±0.0008
298.5	33500	1750	0+1360+400	0.58±0.04	0.0094±0.0018
290	34480	2730	0+2×1360	0.57±0.04	0.0089±0.0015
287	34843	3093	0+2×1360+400	---	---
284	35211	3461	0+2×1360+2×400	0.59±0.08	0.0079±0.0014
275	36360	4610	---	0.53±0.07	0.009±0.002
262	38170	0	0	0.33±0.04	0.004±0.0007
259	38610	440	0+440	0.59±0.08	

Table 3. Assignment of vibrational modes and levels and accompanying photochemical [$\Phi_{PC}(n)$] plus fluorescence [$\Phi_{F}(n)$] yields for 5,6-DMBC at 80 K

Two important general points to stress from the above results are:
(1) relaxation/deactivation occurs only between levels of the same mode, (2) relaxation from the 0 level of an upper state S_X *does not proceed via vibronic levels of any and all lower states.*
Mechanisms have been proposed to try to explain the relatively large yields of PC when there is population of a level of a mode compared to when excitation is to a zero
level.[5,12-13] In general there is agreement that a small barrier is present at the zero levels.

Both nanosecond and femtosecond studies have been carried out on three photoactive chromenes to examine the intramolecular photodynamics.[14] The C-O bond cleavage (see figure 1) occurred within 200-300 fs.[15] The ring opening was faster when exciting at 340 nm compared with 267 nm. The latter wavelength is at or near the zero level of S_3 while the 340 nm wavelength is an upper vibronic level of S_1. Based on all of our results above, a reasonable presumption is that the energy barrier to ring opening is higher in a zero level of a higher energy state than in an upper vibronic level of S_1. Others have also considered their results in terms of competition of vibrational relaxation from upper $S_n$levels with C-O bond breakage.[15]

We will briefly consider two other molecules of quite different character compared with the chromenes but still show both F and PC: 9-bromoanthracene (MBA) and 9,10-dibromoanthracene (DBA).[16] Anthracene (A) was also considered.

At room temperature MBA and DBA exhibit PC only upon excitation into the 2nd electronic transition and the fluorescence intensity is lower than when exciting in S_1. The Φ_{PC} decreases as the temperature decreases and becomes undetectable at 80 K. At 80 K there is a significant dependence of the yield of F on the vibronic level in S_2 for MBA and DBA. We were able to determine the yields of PC as ~0.7 for MBA and ~0.2 for DBA *despite the fact no PC was observed at 80 K.*

	5,6DMBC		7,8DMBC	
	80 K	290 K	80 K	290 K
Φ_F (S_1,0)	0.03	3×10^{-4}	$< 10^{-5}$	$< 10^{-5}$
τ_F	1.5 ns	5 ps	---	---
$k_F{}^0$ (S_1)	2×10^7 s^{-1}	6×10^7 s^{-1}	$\sim5\times10^7 s^{-1}$ [a]	$\sim5\times10^7 s^{-1}$ [a]
$k_{PC}(S_1,0)$	9.3×10^7 s^{-1}	---	$\sim8\times10^{11}$ s^{-1}	---
k_V [b]	$\sim 7\times10^9$ s^{-1}	---	---	---
k_{PC} [b]	$\sim 4\times10^{10}$ s^{-1}	---	---	---
Φ_T	---	no T observed	0.14 [c]	0.14[d]
τ_T	---	---	---	0.84 μs
$\Phi_{NR}(S_1 \rightarrow S_0)$	0.83	---	0.70	---
$k_{NR}(S_1 \rightarrow S_0)$	5.5×10^8 s^{-1}	---	$\sim2.4\times10^{12}$ s^{-1}	---
$\Phi_{IC}(S_2 \rightarrow S_1)$	0.36	---	---	---
$\Phi_{NR}(S_2 \rightarrow S_0)$	0.38	---	0.90	---
$\Phi_{IC}(S_3 \rightarrow S_1)$	0.12	---	---	---
$\Phi_{NR}(S_3 \rightarrow S_0)$	0.55	---	---	---

[a] Assuming $\Phi_F \sim 10^{-5}$ as an upper limit; [b] For the 460 cm^{-1} mode in the S_1 state; [c] Assumes $\Phi_T = 0.14$ as at 290 K; [d] This Φ_T is for a molecule very similar to 7,8DMBC differing only in the 2,2-alkyl substitution

Table 4. Photochemical and Photophysical data for 7,8DMBC and 5,6DMBC at 80 K and 290 K

It was apparent that the radicals produced in the PC process could not migrate out of the solvent cage at 80 K and rapidly recombined[16]. Recall that the F yields exciting into the S_2 state of MBA and DBA showed a dependence on the vibronic level excited. Usually we have been able to associate this phenomenon with competition between PC and vibrational relaxation at each level. However we did not see a dependence of PC upon excitation at two wavelengths/vibronic levels. In addition the yield of F of A showed variation at two different wavelengths/levels of excitation where PC is not expected under the conditions of our experiment. Therefore with the data at hand, the results are consistent with vibrational relaxation being in photophysical competition with intersystem crossing to the triplet manifold for A, MBA and DBA. This is not surprising if as for PC, the k_{ISC} is comparable to k_V as k_{PC} is to k_V.

Summary and Conclusion

1. The criterion necessary to observe results parallel to ours in any molecule is that photochemistry and vibrational relaxation must be in competition at each vibronic level and state that is excited, also see item 10.

2.There is not just one quantum yield of fluorescence (F) or photochemistry (PC), many can exist. These are designated here as $\Phi_F(n)$ and $\Phi_{PC}(n)$. There, in general, can be as many quantum yields as there are vibrational levels <u>and</u> states—5,10,15 or more yields.

3. The source of the multi-quantum yields noted in (2) above is the dependence of the fluorescence yield and photochemistry yield on the specific vibrational mode and level (n) excited—any yield of either (except from a 0 level) is a cumulative number involving all levels through which relaxation occurs.

4. The magnitude of the photochemical yield is largely dictated by the nature of the mode excited, as well as the level within the mode, *not* the energy of excitation.

5. Since the yields of PC depend on the vibronic level excited, the new concepts of Φ_V and Φ_{PC} arise:

$$\Phi_V = k_V / (k_V + k_{PC})$$

and

$$\Phi_{PC} = k_{PC} / (k_{PC} + k_V)$$

Remember, each vibrational mode has its own value of k_V and k_{PC} and therefore, each mode will have its own value of Φ_V and Φ_{PC}. These have no parallel in previously existing experimental or theoretical photophysics/chemistry.

6. In general, relaxation from the <u>0</u> level of an upper state S_X does not proceed via vibronic levels of lower energy states.

Relaxation/coupling may occur between pure excited states and they with S_0.

7. In almost all cases/states, excitation of one quantum of even a low frequency vibration results in a large increase in the PC quantum yield and large decrease in internal conversion from $S_m \cdots S_1 \rightarrow S_0$. This plus large differences in k_{PC} and $k_{PC}(0)$ signifies that there must be a barrier to PC at the 0 level, at least at 80 K.

8.Vibrational relaxation occurs *only between levels of a given mode*- there is no crossing between modes. This is not at all what has been conventionally believed.

9. Based on all of the foregoing, we believe that the *generally accepted mechanism(s) for vibrational relaxation are not at all universally valid.*

10. It is not clear of the generality of the foregoing relative to molecules not undergoing PC. Nonetheless, *it seems completely reasonable that it should be possible for competitive processes* to *vibrational relaxation to occur where similar inherent dynamics are present* such as photoisomerization, photoelectron transfer, proton transfer and intersystem crossing (the latter of which we have seen, *vid**e** infra*).

11. It is clearly possible to alter the efficiency/yield of PC and F of a molecule by judiciously choosing an excitation energy tuned to a particular state or vibrational mode and/or a level within a given mode.

12. It should be possible to even change the nature of the PC in a "photochemically versatile" molecule by changing the mode and/or state that is excited---We predicted this in 1969 and now it has been shown in 1994 and 2001 for ClO_2.

13. The photochemistry and vibrational relaxation yields that are typical of a certain mode, are independent of whether another mode is simultaneously excited (a combination level).

References

1. R. S. Becker and J. Michl, J. Am. Chem. Soc., **88**, 5931 (1966).
2. J. Kolc and R. S. Becker, J. Phys. Chem., **71**, 4045 (1967).

3. R. S. Becker, E. Dolan, and D. Balke, J. Chem. Phys., **50**, 239 (1969). Note that in equation 1, the letter n should be a power symbol.
4. C. Lenoble and R. S. Becker, J. Photochem., **33**, 187 (1986).
5. R. S. Becker, G. Favaro, A. Romani, P. L. Gentili, and F. M. B. Dias, Chem. Phys., **316**, 108 (2005).
6. N. Tyer and R. S. Becker, J. Am. Chem. Soc., **92**, 289 (1970).
7. A. Santiago and R. S. Becker, J. Am. Chem. Soc., **90**, 3654 (1968).
8. R. S. Becker, A. P. Pelliccioli, A. Romani, and G. Favaro, J. Am. Chem. Soc., **121**, 2104 (1999).
9. G. Favaro, A. Romani, and R. S. Becker, Photochem. and Photobiol., **74**, 378 (2001).
10. A. Castellan, J. Kolc and J. Michl, J. Am. Chem. Soc. **90**, 2651 (1978).
11. S. Wallace and J. Michl, Photochem. Photobiol. Proc. Int'l. Conf. 1983; A. H. Zewail, ed; Harwood, New York, Vol 2, 1191 (1983).
12. P. L. Gentili, A. Romani, R. S. Becker and G. Favaro, Chem. Phys., **309**, 167 (2005).
13. A. Migani, P. L. Gentili, F. Negri, M. Olivucci, A. Romani, G. Favaro and R. S. Becker, J. Phys. Chem. A, **109,** 8684 (2005).
14. L. Gentili, E. Danilov, F. Ortica, M. A. Rodgers and G. Favaro, Photochem. Photobiol. Sci., **3**, 886 (2004).
15. Y. Kodama, T. Nakabayashi, K. Segawa, E. Hattori, M. Sakuragi, N. Nishi, and H. Sakuragi, J. Phys. Chem. A, **104**, 11478 (2000).
16. G. Favaro, M. R. di Nunzio, P. L. Gentili, A. Romani, and R. S. Becker, J. Phys. Chem. A, **111**, 5948 (2007).

HISTORICAL NOTE

The 'Belle Epoque' of photochemistry

Angelo Albini,

University of Pavia

angelo.albini@unipv.it

The next few years should be celebrated by photochemists as they can count a hundred years since their discipline came of age. This happened through the work by a few scientists that established photochemistry practically from scratch. In particular, this accomplishment was due to the contribution of two of the major Italian scientists of the beginning of the 20th century, who by a curious coincidence devoted several years each to the chemical reactions caused by light. Their names sound familiar, since most courses on photochemistry in Universities around the world begin by recalling that the Italian scientist Giacomo Ciamician can be considered the father of this discipline, or at least mention his contribution to the photochemistry of ketones, as well as that by Emanuele Paternò, at least for the so-called Paternò-Büchi reaction. Perhaps not everybody is familiar, however, with the figure of these two scientists and appreciates correctly the level that photochemistry had reached before World War I, to a large degree thanks to the work by these two scientists.

Giacomo Ciamician was born to a wealthy family of tradesmen in Trieste (1857) and studied chemistry in Vienna. He then joined the highly reputed Cannizzaro's group in Rome before accepting a chair in Bologna, where he remained almost thirty years until his death in 1922. He founded there a florid school of chemistry that had a prominent role in the development of this discipline in Italy for many years to come and became a leading figure of European science as well as a Senator of the Italian kingdom. Long lasting results from his work are the new finding and rationalization of the chemistry of pyrrole (e.g. the Ciamician-Dennestedt carbene ring enlargement) and of phenol, with the recognition of the common (highly nucleophilic we would say nowadays) character of the reactions of two classes of compounds, as well as the first systematic study of photochemistry, a science that had received very little attention up to that moment (in contrast to photography). His work in this field began when he was in Rome and was preliminarily published in 1886. A more developed presentation of his discoveries was published 14 years later, to be followed by 32 further papers on the chemical effects of light.

The other protagonist, Emanuele Paternò, marquis of Sessa, was born in Palermo in 1847, where he studied chemistry (among the teachers, the young Cannizzaro), and became professor in Torino, Palermo and Rome, where finally succeeded Cannizzaro (he died in 1935). He was possibly the most influential figure of the chemistry of his time in Italy, likewise a Senator of the Kingdom (and for a long time, the vice-chair). During his long career he gave important contributions to both organic and inorganic chemistry, including his series of 11 papers with the bold title 'Synthesis in organic chemistry by means of light' that was published between 1909 and 1914. The are many analogies between the two scientists (which does not mean that there was a good relation between them). Both were influenced by Cannizzaro on one hand and by the great German chemistry of the time on the other, both were national and international leaders. As an example, Cannizzaro, Paternò and Ciamician where consecutively Presidents of the Chemical Society of Rome (which would have become the Italian Chemical Society in 1909) each one for a two-years mandate from 1900 on, and Paternò chaired the first General Assembly of IUPAC in 1920.

The progress of photochemistry in these years can be appreciated by browsing the publications by the protagonists. As it can be seen from the following, most of the reactions discovered have been reported by 1910, although extensions have been published some years later. Thus, in the 2008-2010 period we may celebrate the first 100th birthday of photochemistry as we know it. In fact, as it appears from Fig. 1, at this time photochemistry could count on a large fraction of the main processes known today. Several decades had to elapse before such a large number of reactions could be discovered (in part indeed rediscovering the results of that time that had been forgotten in the meantime, as it is the case for the synthesis of oxetans). Below are indicated the accounts and a choice of the key publications.

Accounts

1902	First preliminary account by Ciamician of his research on photochemistry and the motivation for using light in organic synthesis (G. Ciamician and P. Silber, *Gazz. Chim. It.*, 1902, **32**, 208).
1908	Text of a talk presented by Ciamician in Paris, essentially all of the photochemical reactions he discovered (see Fig. 1 for some of the most important of such reactions) and role of photochemistry as a milder alternative to the usual methods, close to the mild conditions of reactions in living organisms (*Bull. Soc. Chim. France [4]*, 1908, i.).
1908	Text of a talk presented by H Stobbe (professor in Leipzig, studied isomerization reactions, such as the photochromism of fulgides) in Vienna. He again recognizes that photochemistry is far from the development it should have, while evidencing the role of Ciamician's research. He is convinced that more work by organic chemists is required, more reactions have to be discovered (*Zeitsch. Elektroch.*, 1908, **33**, 173)..
1909	Review on the state of the art of photochemistry, by Paternò; he recognizes that very little had been done before the work by Ciamician and Silber (*Gazz.Chim. It.*, 1914, **44**, 31).
1912	Text of a talk presented by Ciamician in New York: role of photochemistry in synthesis and as a means for exploiting the abundant and renewable energy from solar radiation, by means ranging from an improved agriculture to photovoltaics (*Science*, 1912, **36**, 385).
1914	Final review of own work by Paternò, who insists on the synthetic aspects (C-C bond formation) he had evidenced in the photochemical reactions before Ciamician (*Gazz.Chim. It.*, 1914, **44**, 31).

Some of the research papers

1886	Preliminary announcement by Ciamician of his discovery that quinone and nitrobenzene are reduced upon irradiation in alcohols (*Gazz. Chim. It.*, 1886, **16**, 111; *Gazz. Chim. It.*, 1886, **16**, 536, starting from the second one the Authors are always G. Ciamician and P. Silber).
1900	Again a preliminary paper on the photochemical reduction of quinones and ketones, more expanded. The title is Chemische Lichtwirkungen, Chemical effects of light, and this can be considered no. 0 of Ciamician and Silber series (*Ber. Dtsch. Chem. Ges.*, 1900, **33**, 2911).
1901	Full paper on the photochemistry of quinones and ketones in alcohol solution, no. 1 of the series (*Ber. Dtsch. Chem. Ges.*, 1901, **34**, 1530).
	No. 2 of the series, Photorearrangement of *ortho*-nitrobenzaldehyde to *ortho*-nitrosobenzoic acid (*Ber. Dtsch. Chem. Ges.*, 1901, **37**, 2040).
1902	No. 3 of the series, photochemical reduction of nitrobenzene in alcohols (*Ber. Dtsch. Chem. Ges.*, 1902, **35**, 1992).
	No. 4 of the series, dependence of photochemical reactions on the irradiation wavelength, (*Ber. Dtsch. Chem. Ges.*, 1904, **37**, 3593).
	No. 5 of the series, photodimerization of cynnamic acid, stilbene, coumarin (*Ber. Dtsch. Chem. Ges.*, 1902, **35**, 4128).
1903	No. 6 of the series, photochemical coupling between benzaldehyde or benzophenone and alcohols; □-cleavage of ketones (*Ber. Dtsch. Chem. Ges.*, 1903, **36**, 1575).
	No. 7 of the series, again on dimerization reactions, *Ber. Dtsch. Chem. Ges.*, 1903, **36**, 4266.
1905	No. 8 of the series, photochemical reaction between nitrobenzene and benzaldehyde (*Ber. Dtsch. Chem. Ges.*, 1905, **38**, 1176).

1907 No. 11 of the series, photohydrolysis of aliphatic ketones, $Me_2CO + H_2O \rightarrow CH_3COOH + CH_4$ (*Ber. Dtsch. Chem. Ges.*, 1907, **40**, 2415). .

1908 No. 13 of the series, 2+2 intramolecular cyclization of carvone, α-cleavage of dihydrocarvone (now known as Norrish Type I reaction) (*Ber. Dtsch. Chem. Ges.*, 1908, **41**, 1928).

1909 Paternò begins to report his photochemical research. He will later claim that all of his work was essentially complete in this year and ask for priority at this point. For the moment, in two wonderful papers he describes the reaction between ketones (or aldehydes) and alkenes and assign the correct formulae to the products, the oxetans (now known as Paternò-Büchi reaction). This are No. 2 and 3 of his series on 'Synthesis in organic chemistry by means of light' (E. Paternò and G. Chieffi, *Gazz. Chim. It.,* 1909, **39**, 341 and E. Paternò, F. Traetta-Mosca, *Gazz. Chim. It.,* 1909, **39**, 449).

1910 No. 16 of Ciamician series, with the photochemistry of aliphatic ketones in alcohols; the occurring of cross coupling ($Me_2CO + CH_3OH \rightarrow (CH_3)_2C(OH)CH_2OH$) is evidenced. This is a novel way of making a carbon-carbon bond that can be likened to the aldol condensation but does not require a base (*Ber. Dtsch. Chem. Ges.*, 1910, **43**, 945).

No. 18 of Ciamician series, aromatic ketones and alkyl aromatics give, among other products, bibenzyls (*Ber. Dtsch. Chem. Ges.*, 1910, **43**, 1536).

No. 4-6 of Paternò series, reaction of aromatic ketones with alkylbenzenes (the formation of cross-coupled products is an important feature), with ethers and with esters, E. Paternò and G. Chieffi, *Gazz. Chim. It.,* 1910, **41**, 321 and 415 and E. Paternò and G. Forli-Forti, *Gazz. Chim. It.,* 1909, **39**, 332.

1911 No. 19-21 of Ciamician series, extension on the photochemistry of ketones, both intra- and intermolecular (*Ber. Dtsch. Chem. Ges.*, 1911, **44**, 1558, 1154 and 1158).

1913 No. 25 of Ciamician series, benzene is essentially photostable even in the presence of oxygen, but alkylbenzenes are oxidized to phenyl ketones or benzoic acids (auto-oxidation). Oxidized are also aryl olefins (*Atti Acad. Lincei*, 1913, **22**, 127).

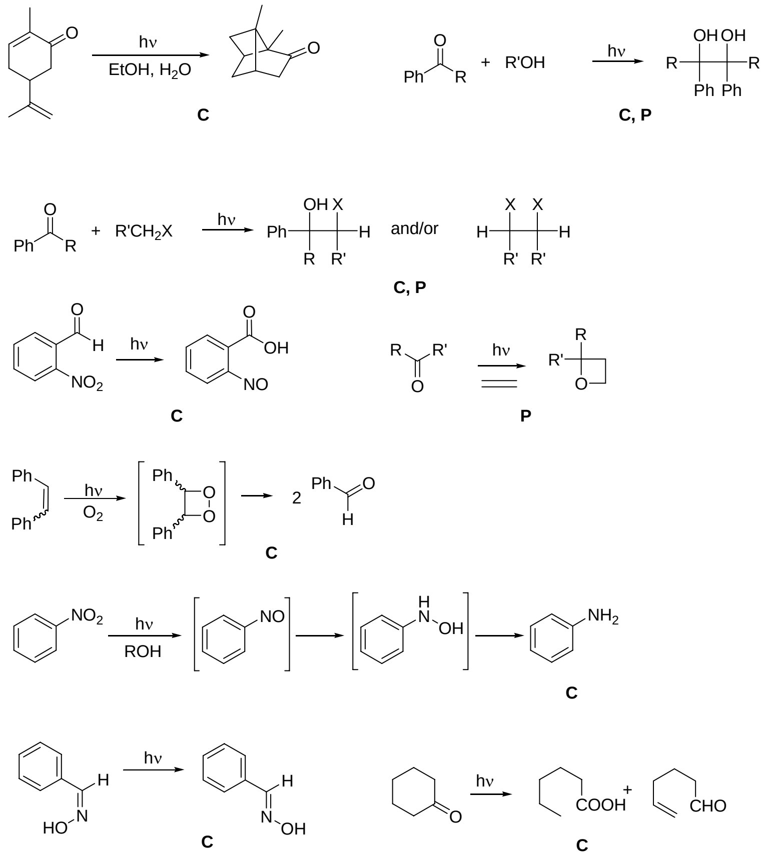
1914 No. 29 of Ciamician series, α-cleavage of ketones under oxygen gives acids, a mild analogue of the permanganate oxidation (*Ber. Dtsch. Chem. Ges.*, 1914, **47**, 640).

No. 8-10 of Paternò series, photochemical reaction of ketones with ammonia and amines (E. Paternò, *Gazz. Chim. Ital.* 1914, **44**, I, 151 and 237, II, 99. No 11 of this series is the account mentioned above, the last paper of his series.

1915 No. 31-33 of Ciamician series, auto-oxidation of nicotine and some amines, as well of some ketones (*Ber. Dtsch. Chem. Ges.*, 1915, **48**, 181, 187, 190). The last paper is an answer to some criticism by Paternò. This ends the series on the chemical effects of light by Ciamician and Silber.

Considering the list of the two series of papers, the short time span involved, the variety of reactions discovered (have a look to the reactions in Scheme 1) and the fact that only two groups worked at it, one can but be impressed. Europeans should be proud of this important contribution of their scientists, really on the forefront of the science of that time.

Reading the papers of the above series is a nice experience even nowadays, because one can appreciate the careful work needed for separating the products and for recognizing their structure with the poor means then available. As an example, when studying the reaction of ketones with alkenes, Paternò arrives at the correct formula of the oxetan for the product on the basis of elemental analysis and by considering that: the product does not give alcohol or ketone tests; the reaction is reversible at high temperature; the density and the refractive index of the product fits with that of oxygenated compounds with an ether structure rather than with a ketone structure.



Scheme 1. Photochemical reactions studied by Ciamician and Silber (**C**) and by Paternò (**P**).

Several studies have been devoted to the history of photochemistry and the role Ciamician, Silber and Paternò had in getting this discipline started, as indicated below.[1-8] Other are in preparation.

1. H. D. Roth, Twentieth century developments in photochemistry. Brief historical sketches, *Pure Appl. Chem.* 2001, **73**, 395-403.

2. H. D. Roth, Selected developments in the 20th century photochemistry: Historical sketches, *EPA Newsletter* 2001, **71**, 37-57.

3. H. D. Roth, The origins of organic photochemistry, *Angew. Chem.* 1989, **101**, 1220-34.

4. H. D. Roth, Organic photochemistry one hundred years ago, *EPA Newsletter* 1988, **32**, 1-22.

5. A. Albini and M. Fagnoni, Green chemistry and photochemistry were born at the same time, *Green Chem.*, 2004, **6**, 1-6.

6. A. Albini and M. Fagnoni, 1908: Giacomo Ciamician and the concept of green chemistry, *ChemSusChem*, 2008, **1**, 63-67

7. G. Nebbia, G .B. Kauffman, Prophet of solar energy: A retrospective view of Giacomo Luigi Ciamician (1857-1922), the founder of green chemistry, on the 150th anniversary of his birth, *Chem. Ed.* 2007, 12, 362-369.

8. V. Balzani, A. Credi, M. Venturi, Photochemical conversion of solar energy, *ChemSusChem* 2008, 1, 26-58

PUBLICATIONS

Abstracts of Theses in Photochemistry

Fiona DICKINSON

Unusual Mechanisms of DNA Damage Caused by Cyanine Dye Photosensitization

PhD Thesis (December 2007)
Newcastle University

The aims of this work were to elucidate the multi-step pathway of DNA cleavage photosensitized by asymmetric cyanine dyes, and to definitively deduce the mechanism that results in the previously reported unusually high yield of double strand breaks.

The dyes YO and its dimer YOYO are used extensively in high sensitivity applications such as detection of DNA on electrophoresis gels, single molecule microscopy, and solution assays. However, these dyes have been shown to both photobleach and photocleave DNA especially when used at the high dye loadings and light intensities used for the visualization of single molecules. Previous studies have reported that the rate of double strand break (dsb) formation by YOYO is unusually high, and have established that this is not simply a result of dimerisation since YO also produces dsbs. This thesis explores the photochemistry behind this observation.

Chapter 1 provides an introduction to the work and reviews mechanisms of damage and cleavage of DNA, focusing on damage caused by reactive oxygen species (ROS) and one electron oxidation. It also summarises the DNA binding and photochemical and photophysical properties of the asymmetric cyanine dyes.

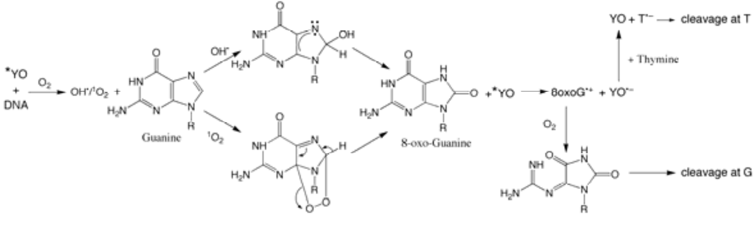
Chapter 2 provides an overview of the techniques used in this work.

The first results chapter, Chapter 3, examines relaxation cleavage assays and sequencing studies with emphasis on the effect of specific and non-specific scavengers. This provided a picture of the apparent role of both ROS and electron transfer (ET) in producing strand breaks. Cleavage was shown to occur primarily at 5’-GG sites, which is characteristic of electron-transfer induced cleavage, even though singlet oxygen ($^1O_2$) and hydroxyl radicals ($OH^\bullet$) were implicated in the rate-limiting step. This suggests that the initial reactions were not immediately responsible for the reaction products, and that complex reaction pathways were involved.

Chapter 4 shows that either $^1O_2$ or $OH^\bullet$**,** or both species are generated by the dyes in the presence and absence of DNA, depending upon conditions. By examining the lifetime of $^1O_2$, its quantum yield of production was determined. $^1O_2$ can interact with both YO and YOYO as well as DNA.

Chapter 5 examines the effect of including the modified bases 7,8-dihydro-8-oxodeoxyguanosine (8-oxodG) and 7,8-dihydro-8-oxodeoxyadenosine in oligonucleotide DNA on the absorption, fluorescence, and fluorescence lifetimes of YO and YOYO. The presence of 8-oxodG was shown to strongly quench the emission of the dyes. The steady state and lifetime quenching by 8-oxodG is discussed in the context of an ET model for the oligonucleotides, based on Marcus theory.

The final results chapter, Chapter 6, examines the role that thymine plays in the photofading and photobleaching of YO and YOYO. DNA containing alternating GC base pairs was shown to exhibit the most dramatic loss of fluorescence upon irradiation, whereas DNA containing all bases was shown to induce the most rapid loss of absorption. This is interpreted in terms of a model in which thymine has a role in the production of double strand breaks via its interaction with the dye, *i.e.*:



Maria ABRAHAMSSON

Tuning of the excited state properties of ruthenium (II) polypyridyl complexes

PhD thesis, Uppsala University, December, 2006
Working place: Department of photochemistry and molecular science, Uppsala University, Box 523, 75120 Uppsala, SWEDEN
Present working place: Department of Chemistry, Johns Hopkins University
Supervisors: Prof. Leif Hammarström, Dr. Hans-Christian Becker

The main theme of this thesis is tuning of the excited state properties of Ru(II)-polypyridyl complexes, and more specifically to prolong the excited state lifetime of the geometrically favorable bis-tridentate type complexes, *without* a concomitant decrease of the excited state energy. Since many attempts to increase the excited state lifetime of bis-tridentate Ru(II)-complexes have resulted in a substantial lowering of the excited state energy, thus also reducing its reactivity, a new strategy to extend the excited state lifetime was outlined, investigated and proven to be successful.

The strategy is based on the idea that a more octahedral coordination can destabilize the metal e_g orbitals, thus leading to a higher energy for the ^{3}MC state which is responsible for a large part of the room temperature non-radiative decay of tris-bidentate Ru(II)-complexes in general. This would lead to a slower transition from the emissive ^{3}MLCT to the ^{3}MC states, resulting in the desired longer lifetime of the ^{3}MLCT state.

In our first generation of photosensitizers, a 50-fold increase of the excited state lifetime, compared to the parent $[Ru^{II}(tpy)_2]^{2+}$ was obtained, clearly showing that ligands with better bite angles, *i.e.* more close to octahedral, induce a destabilization of the ^{3}MC energy and thus give the desired longer excited state lifetimes of the ^{3}MLCT state. A second generation of photosensitizers resulted in even longer excited state lifetimes, around 1 microsecond. Finally, the third generation of photosensitizers showed an almost octahedral coordination around the Ru center, and excited state lifetimes ranging from 0.4 to 5.5 microseconds, which is an increase of around four orders of magnitude compared to the parent $[Ru^{II}(tpy)_2]^{2+}$ complex. This makes them able to out-compete the widely used $[Ru^{II}(bpy)_3]^{2+}$ complex, which have excellent photophysical properties but often fail to provide opportunity for constructing linear donor-photosensitizer-acceptor arrays.

Temperature dependent excited state lifetime measurements were performed on two complexes in each generation. The results obtained confirmed that the deactivation via ^{3}MC states was significantly decreased and thus, this finding further supports the conclusion that our strategy is successful. In addition, all the complexes in the third generation allows for symmetric substitution that can be used for construction of linear supramolecular assemblies, which is interesting in many areas where charge separation is crucial such as artificial photosynthesis, photovoltaics and molecular electronics. The reactivity towards bimolecular electron and energy transfer was proved with methyl viologen, TTF and diphenyl-anthracene as quenchers for the third generation of complexes. Finally the complexes in the third generation show remarkable photostability. The excellent properties of the complexes in the third generation make them useful for many applications.

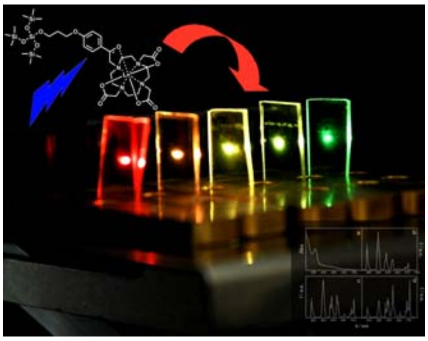
Gianluca ACCORSI

Trivalent Lanthanide Ions: Luminescence and Applications

PhD thesis, University of Bologna, March, 2007
Working place: Molecular Photoscience Group lab., ISOF-CNR
Via P. Gobetti, 40129, Bologna, Italy
Supervisor: Prof. Alberto Juris

Supplying sustainable energy to a planet populated by 9-billion people by mid-century, is definitely one of the most urgent problems that our civilization is currently facing. In the less developed regions of the world, billions of people have the right to aim at higher standards of living and try to follow the developing model of the Western world. At the same time, the most affluent countries continue to increase their economic wealth, according to statistics. This trend is hardly sustainable in the mid-long term. In particular, the ever increasing demand of energy cannot be satisfied by mainly employing fossil fuels due to the known problems of supply, pollution and climate change. In this scenario, an increasing role of renewable energies and an improvement in energy efficiency are mandatory. New materials, innovative technologies and smart devices are key ingredients to find solutions to these challenges, and secure a good and sustainable standard of living for the generations to come.

The work presented here tries to give a contribution in the above mentioned direction since discusses the light induced properties of several trivalent lanthanide (Ln) complexes which are of interest for some applications such as efficient lighting, broadband telecommunication, bioassay, *etc.* Both organic ligands and *d*-block metal complexes have been used as coordinating/sensitizer units for the central lanthanide ions. Luminescence efficiencies up to 50% and appreciable emission intensities have been detected in the visible (Vis) and near infrared (NIR) spectral regions, respectively. The photophysical investigations have been carried out in solution and in solid state. Different polarity and deuterated solvents have been employed for a



Tunable light from Eu(III) and Tb(III) (red → green) complexes covalently linked to glass surfaces through Sol-gel technique.

better understanding of the involved photoinduced processes and to probe the coordination environment, respectively. To simulate the PL properties of the luminescent materials in devices, also doped solid matrices have been investigated. Sol-gel glasses[1], polymer and, with an original approach, single walled carbon nanotubes[2] (SWCT) have been employed to link or trap the Ln(III) complexes. Intense, tunable (Eu and Tb, red → green) and monochromatic (red, Eu) light resulted from doped SiO_2 and adsorbed SWNT matrices, respectively. The simplicity of the fabrication processes encourages to improve both the chromophores and hosting materials for applications in efficient lighting technologies such as (W)OLED. An overview on the abundance and resources, applications and spectroscopic properties of the rare earths elements (REE) is also reported in the introductory section.

[1] Armelao, L.; Bottaro, G.; Quici, S.; Cavazzini, M.; Raffo, M. C.; Barigelletti, F.; Accorsi, G. *Chem. Commun.* **2007**, 2911.

[2] Accorsi, G.; Armaroli, N.; Parisini, A.; Meneghetti, M.; Marega, R.; Prato, M.; Bonifazi, D. *Adv. Funct. Mater.* **2007**, *17*, 2975.

Jacob BAGGERMAN

Photoactive Hydrogen-Bonded Rotaxanes

PhD thesis, University of Amsterdam, June 30, 2006
Working place: Van ‘t Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands
Supervisor: Fred Brouwer

The rotaxane architecture, which consists of a macrocyclic ring (wheel) trapped on a thread-shaped molecule (axle), is very suitable for the design of molecular motor molecules, in particular molecular shuttles. In the present study fluorescent rotaxanes were synthesized and studied under different experimental conditions, and the dynamics of newly designed molecular shuttles were investigated.

The synthesis of new fluorescent rotaxanes containing perylene diimides in the axle was accomplished in collaboration with the group of professor Vögtle (Bonn, Germany). The absorption and fluorescence spectra of these rotaxanes are red shifted due to the hydrogen bonding interaction between the wheel and the imide. The influence of the different types of solvent/solute interactions on the absorption and fluorescence spectra is analyzed with the Kamlet-Taft expression. The reduction potentials of the rotaxanes are shifted to higher values because the macrocycle stabilizes the radical anions and dianions more than the neutral molecules. The hydrogen bonding interaction also results in changes in the absorption spectra of the rotaxane anion and dianion in comparison with those of the axle. The observed fluorescence decay times of the rotaxanes are consistently shorter than those of the axle. Single molecule fluorescence measurements (in collaboration with professors De Schryver and Hofkens, Leuven, Belgium) revealed the distributions of emission maxima and decay times of the rotaxanes in polymer films. The observed red-shifts make the perylene diimide a suitable chromophore for sensing the interactions with the nearby wheel (Chem. Eur. J. (2007), 13, 1291-1299).

The properties are described of a naphthalimide rotaxane attached to an acid-terminated self-assembled monolayer on a gold surface. The fluorescence of such a (sub)monolayer of molecules on a gold substrate can be difficult to detect because of the small number of molecules in the sample and the partial quenching of the fluorescence by the gold. Nevertheless, it was shown that it is still possible to detect the fluorescence of the two fluorophores under these conditions. The fluorescence spectra of the amino naphthalimide on the surface are similar to those of the compound (in its protonated form) in acetonitrile solution. In the case of the rotaxane the fluorescence from the monolayer is red-shifted compared to that in solution. The red-shift is attributed to hydrogen bonding between the acid groups of the SAM and the carbonyl groups of the imide (J. Phys. Chem. B, (2004), 108, 15192-15199).

Finally, the kinetics of photoinduced motion in new photoresponsive molecular shuttles were studied. In these systems different diimides were used as stations that can be switched between the neutral and radical anion forms. In the latter, the macrocyclic ring binds to the diimide (J. Am. Chem. Soc., (2008), 130, 2593-2601).

Implications for the effects of the structure on the previously postulated shuttling mechanism are discussed.

Radim BERANEK

From Photocatalysis to Optoelectronic Switches: Studies of Visible Light Active Photoelectrodes Based on Surface-Modified Titanium Dioxide

PhD thesis, University of Erlangen-Nürnberg, July, 2007
Working place: Institut für Anorganische Chemie, Egerlandstr. 1
D-91058 Erlangen, Germany
Supervisor: Horst Kisch

Semiconductors enable efficient light-induced generation and separation of charges which can subsequently undergo redox reactions with substrates or induce a photocurrent. This opens up a route to various applications in photocatalysis, photovoltaics, sensor technology, biomedicine and optoelectronics. Obviously, in order to achieve optimal performance, semiconductors with well-tailored optical and photoelectrochemical properties are required in most applications. The development of methods allowing control of these semiconductor properties attracts therefore significant interest.

This thesis presents investigations of a novel type of visible light active TiO_2 materials – TiO_2 surface-modified with nitrogen species. It is shown that both films and powders can be easily modified by a heat treatment in the presence of urea pyrolysis products. The surface modification consists in incorporation of nitrogen species containing carbon (atomic ratio N/C ~ 2) into the surface of TiO_2 and can be used for tuning its fundamental optical and photoelectrochemical properties – the optical absorption edge and the energy position of the band edges – in a systematic manner.

In general, the modification leads to a significant red shift of the optical absorption edge. At the same time an anodic shift (by ~ 0.2 – 0.3 V) of the quasi-Fermi level of electrons was observed for all modified materials. The electrodes based on the surface-modified

TiO_2 materials exhibited a significant photocurrent response upon visible light irradiation down to 700 nm. The efficiency of photocurrent response is also highly dependent on the redox properties of the electrolyte since the photogenerated holes are trapped in deep intra-bandgap surface states before they react with the reducing agent in the electrolyte. In aqueous electrolytes this leads to enhanced recombination unless more easily oxidizable species like iodide are present.

Furthermore, the surface-materials can be employed for fabrication of photoelectrodes exhibiting wavelength-controlled switching of photocurrent direction. The electrode is a hybrid assembly of two simple inorganic semiconductors – surface-modified TiO_2 (n-type semiconductor) and CuI (p-type) – deposited on an ITO-glass. Under optimized conditions an unusually sharp change in photocurrent direction occurs in the range of 410 – 420 nm. The switching mechanism is based on well-fitting electrical (n-/p-type), optical (bandgap) and photoelectrochemical (band edge positions) properties of the nanocrystalline materials used. This approach opens up a route to fabrication of further optoelectronic switches of desired features by simply combining materials with optimized optical and photoredox properties.

Christophe CANTAU

New materials for visible-light photocatalysis: from elaboration to implementation.

PhD thesis, University of Pau et des Pays de l'Adour, December 2006
Working place: Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM), UMR CNRS 5254, Université de Pau et Pays de l'Adour
Hélioparc Pau-Pyrénées, 2 rue du Président Angot, 64053 PAU cedex 9, France.
Supervisor: Sylvie LACOMBE and Thierry PIGOT

The quality of the air we breathe has become a major concern of society. More particularly, the quality of indoor air worries specialists because concentrations of contaminants are higher indoors and we spend approximately 80 % of our time in closed places (houses, schools, offices, transport). Besides controlling and reducing source emissions (ex: HQE® processes for buildings), it is essential to eliminate this pollution.

Our contribution to this field focuses on evaluating the efficiency of a novel photooxidation process, based on hybrid materials sensitized by visible light. These materials are made up of a silica "xerogel" matrix, on which aromatic photosensitizers (AP), selected from their activity in conventional oxidation reactions in solution, are adsorbed, grafted or co-condensed. These materials have to be transparent, porous, stable and easy to use. Different AP/xerogel combinations were studied for the photooxidation at the gas-solid interface of a model contaminant, dimethylsulphide (DMS). We also tested the activity on other, more difficult to oxidize pollutants, such as disulphide, thiol and toluene. It could be demonstrated that these hybrid materials were good producers of singlet oxygen: the quantum yield of singlet oxygen production, as well as singlet oxygen lifetimes, were determined directly inside the xerogels.

During this study, a new photosensitizer (*X, patent applied for*) was synthesized. It combines good photo-oxidizing properties and easy functionalization, allowing convenient grafting on different supports. Overall, all the materials studied were very efficient for DMS oxidation, and some AP's were active against disulphide compounds or toluene. *X*-based materials, synthesized by a co-condensation process, were particularly promising. They were activated by visible light and were easily regenerated by washing at the end of the reaction.

The efficiency of these materials was compared to that of more conventional TiO_2 photocatalysts. In this respect, some attempts were made to shift the absorption band of titanium dioxide (TiO_2) towards visible part of the spectrum by doping with nitrogen. Characterization of these TiO_2 powders led to some indications on the nature of TiO_2 doping. The efficiency of these modified TiO_2

under visible light was evaluated by photooxydation experiments in solution.

Stéphanie DEROO

Photochemistry of photooxidant Ru(II) complexes in presence of amino acids or anchored on oligonucleotidic probes and on biodegradable polymers

PhD thesis, Université libre de Bruxelles, November, 2006
Working place: Organic Chemistry & Photochemistry, CP 160/08, 50 avenue F.D. Roosevelt, 1050 Brussels, Belgium
Supervisor: Andrée Kirsch – De Mesmaeker & Cécile Moucheron

Biologically photoactive metal complexes are considered as novel interesting potential drugs because they offer the advantage, over that of classical transition metal-based drugs, to be triggered only under illumination.

We have shown that Ru(II) complexes bearing at least two TAP ligands (TAP = 1,4,5,8-tetraazaphenanthrene) are able to form a covalent photoadduct on the guanine nucleic base, which could lead to the inhibition of cellular processes *in vivo*. However, applications of these photoreactive complexes are hindered by several obstacles: (i) the photoadduct formation is not sequence specific, (ii) the complexes are unable to penetrate cells membranes and (iii) their photochemical behaviour in presence of other cellular components is not well-known. These three distinctive aspects were investigated in this work.

We have developed an efficient new anchoring method of photoactive Ru(II) complexes based on the chemoselective oxime linkage. On the one hand, the metallic compounds were tethered to oligonucleotidic probes, which confer specificity to the photoreaction thanks to their hybridization properties. The photocrosslinking of oligonucleotidic duplexes by photoadduct formation was evidenced by several techniques and different parameters have been investigated such as the photostability and photooxidizing power of the attached complexes and the length of the linker. On the other hand, biodegradable polymers were linked to the complexes to be further used as cellular vectorizing agents. We have shown that the large tethered polymer (6 kDa and 80 kDa) induces weak effects on the luminescence properties of the Ru(II) complexes and that these latter are still able to photooxidize guanine residues and to lead to the formation of photoadducts with guanine-containing oligonucleotides. As the presence of the polymer does not prevent the photodamaging of the oligonucleotides by the complexes, the uptake of these Ru-conjugates by cells will be investigated in the future. Finally, we have studied free photoactive complexes in presence of L-tyrosine and related compounds. The luminescence of the photooxidizing Ru(II) complexes is quenched by these tyrosine containing compounds and formation of photoproducts has been demonstrated by different techniques, for example Ru(II) complex bearing a tyrosine unit as ligand. Such a product, resulting from a dechelation-rechelation process, is interesting because it could be observed with different proteins that contain tyrosine.

Mattias P. ENG

Triplet excitation energy transfer in Donor-Bridge-Acceptor systems: experimental and theoretical investigations

PhD thesis, Chalmers University of Technology, September, 2007
Working place: Department of Chemical and Biological Engineering/Physical Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden
Supervisor: Bo Albinsson

This thesis is a contribution to the understanding of bridge mediation of electron exchange processes in Donor-Bridge-Acceptor (D-B-A) systems. The field of research is relevant for the development and optimization of dye-sensitized solar cells, artificial photosynthesis, and the possible future development of molecular electronic devices. First an investigation of gold(III) porphyrins, commonly used as donors and acceptors in D-B-A systems, is presented. Then an experimental and theoretical investigation of the influence of several system parameters on triplet excitation energy transfer (TEET) ensues. Finally, the work aims for future applications with the characterization of self-assembled monolayers (SAMs) of OPE structures, commonly used as bridges in D-B-A systems, on gold.

The main focus of this thesis is to investigate what governs the bridge mediation of TEET in D-B-A systems. The investigation starts with an experimental study of TEET in a series of D-B-A systems, where a zinc(II) porphyrin acts as the donor and the corresponding free-base porphyrin acts as the acceptor. The donor and acceptor chromophores are separated by oligo-p-phenyleneethynylene bridge units where the number of phenyleneethynylene groups varies between 2 and 5. The experiments are supported by a large number of theoretical calculations, leading to a model for the conformational dependence of the electronic coupling that reproduces the experimentally determined temperature dependence of the bridge mediation. In a parallel, purely theoretical, investigation, the bridge mediation of the electronic coupling for TEET is found to depend on the energy gap between relevant states, ΔE_{DB}, and the donor-acceptor separation, R_{DA}, in accordance with the McConnell model. The applicability of this model to systems with conjugated bridges is discussed and examples of systems where the model does not apply are identified. For these systems an alternative model, based on electron tunneling through a square barrier, first derived by Gamow, is found to qualitatively describe the data. A more elaborate version of this model is found to accurately describe both the dependence of donor-acceptor separation and donor-bridge energy gap on the electronic coupling for experimental data from literature. The advantage of this model is that it will potentially allow for the use of molecular properties of the individual building blocks, available from experiments and/or calculations, to predict the properties of D-B-A systems.

Fábio FERNANDES

Biophysical Studies of Membrane Proteins/Peptides. Interaction with Lipids and Drugs.

PhD thesis, Instituto Superior Técnico, September, 2007
Working place: Centro de Química-Física Molecular. Complexo Interdisciplinar. Instituto Superior Técnico. Av. Rovisco Pais 1049-001 Lisbon. Portugal.
Supervisor: Manuel Prieto

Biomembranes are responsible for the performance of multiple cellular functions and the multiplicity of these tasks requires a complex chemical composition. While the structural framework of biomembranes is the lipid bilayer, other components, notably proteins, are present. These distinct components present different energies of interaction, leading to heterogeneous lateral distribution in the membrane.

In this work, the interactions between the components of biomembranes in several different systems were studied. The lateral distribution of major coat protein (mcp) of the M13 bacteriophage was shown to be highly dependent on the lipid composition of the membrane. A new methodology for quantification of protein-lipid selectivity was also developed and applied with success to the mcp.

Protein-drug binding studies were performed following different approaches. To the study of binding of a V-ATPase inhibitor to a selected transmembrane domain of the enzyme, a reductionist approach was considered, while in the case of binding of ciprofloxacin to OmpF, the intact protein was used.

The interaction of an N-terminal amphipatic segment of a BAR domain with membranes was also investigated and insight was achieved on the possible role of this segment in membrane remodelling. Finally, the hypothesis of spontaneous clustering of phosphatidylinositol-(4,5)-bisphophate was tested and ruled out.

Eduard FRON

Femtosecond Transient Absorption of Donor-Acceptor Systems

PhD thesis, K.U. Leuven, Belgium, December 2007
Working place: Laboratory for Photochemistry & Spectroscopy, Chemistry Department, K.U.Leuven, Celestijnenlaan 200 F, 3001 Heverlee, Belgium
Supervisors: **Prof. Dr. F. C. De Schryver** and **Prof. Dr. M. Van der Auweraer**

The results presented in this thesis concern the photophysical properties of several perylenemonoimide functionalized penthaphenylene systems in solution. The experimental investigation of the excited state dynamics performed by means of the ultrafast laser spectroscopy revealed the occurrence of electron and energy transfer. These processes lead to the formation of excited state intermediates with distinct photophysical properties.

An experimental and systematic study on time-dependent spectral properties of a rigid, extended system consisting of one [**PI-(pPh)$_1$-PI**], two [**PI-(pPh)$_2$-PI**] and three [**PI-(pPh)$_3$-PI**] pentaphenylene units end-capped with perylenemonoimide is presented. These systems are investigated in detail by femtosecond transient absorption and single photon timing experiments and compared to analogous model systems. Exciton-exciton annihilation occurs in both **PI-(pPh)$_1$-PI** and **PI-(pPh)$_2$-PI** systems investigated upon high power excitation. These results are in line with the kinetic results obtained for **PI-(pPh)$_3$-PI** and show that the annihilation becomes faster and more efficient as the exciton coupling increases. The annihilation was found to promote one chromophore into a higher excited singlet state which then rapidly relaxes to S_1 via a charge transfer state intermediate. Starting from the higher excited state the **PI** radical anion is formed even in a low polar environment and decays with a time constant of about 1 ps. The mechanism observed suggests an elegant way to explore reactions in the upper excited states, as in this case an ultrafast charge transfer occurred above the lowest singlet excited state. For the largest system **PI-(pPh)$_3$-PI, t**he experiments demonstrated that a CT-CT annihilation takes place after formation of two independent charge transfer-like states. This novel excited state interaction was observed in a solvent of medium polarity by comparing the transient decay traces recorded with five different excitation powers. Based on quantum-chemical calculations the **PI** excited state wavefunction was found to significantly spread over the neighboring pentaphenylene skeleton in polar solvents. This leads to a shorter center-to-center separation between the two **PI** transition dipoles. Both theoretical and experimental results furthermore yield a larger overlap between the excited state emission and absorption spectra upon increasing the solvent polarity.

The excited state properties of **PI-(pPh)$_1$** and **PI-(pPh)$_2$** are further explored using pump-re-pump-probe and pump-dump-probe transient absorption technique in the visible region. This technique allowed gaining new insights of the dynamics of the excited states. For instance, upon pre-exciting the **PI** subunit an additional relaxation pathway is revealed in the deactivation process of the **pPh**. By appropriate selection of wavelength and timing, the extra pulse initially promotes the energy acceptor into an excited state thereby opening a new pathway in transferring the excitation energy from the **pPh** to the excited state.

Alexandre FÜRSTENBERG

Ultrafast Excited-State Dynamics in Biological and in Organised Environments

PhD thesis, University of Geneva, January 2008
Working place: Département de chimie physique, Université de Genève
30 Quai Ernest-Ansermet, 1211 Genève 4, Switzerland
Supervisor: Eric Vauthey

The way and the rate at which excited chromophores relax back to their initial state strongly depend on their local molecular environment. The highly organised nature of biological macromolecules such as proteins or nucleic acids makes biomolecular environ-ments very special. This thesis work aims at contributing to a better understanding of how organised macromolecular environments affect the relaxation dynamics of excited fluorophores and in particular ultrafast processes such as dynamic solvation, vibrational energy relaxation, fluorescence quenching, or fluorescence depolarisation. A comprehensive picture of the influence of biological environments on the dynamics of excited chromophores would enable the use of selected molecular probes to infer new knowledge on systems as well as the development of innovative routes to access very local – structural for example – information spectroscopically. Tunable molecular systems belonging to three major classes of biological environments, namely proteins, nucleic acids, and lipids, were thus studied with the help of specific fluorescent probes and optical steady-state and time-resolved spectroscopy.

The influence of a protein environment on the dynamics of excited fluorophores was investigated by coupling selected probes to biotin, a small molecule which very tightly and selectively binds to the proteins avidin and streptavidin. The investigations confirm that the solvation dynamics is partially slowed down by more than one order of magnitude when a chromophore is located at a protein interface compared with a bulk water environment. Furthermore, for the first time, the vibrational energy relaxation dynamics of a probe at a protein interface could be followed by time-resolved fluorescence spectroscopy.

The excited-state dynamics in nucleic acid environments was followed by using oxazole yellow dyes, the photophysics of which was studied in details in bulk solvent and when bound to DNA, RNA, or mixed DNA-LNA strands. It was established that not only one, as postulated so far, but two mechanisms control the strong fluorescence contrast observed between the free and bound forms of the dyes and the intimate relationship between their molecular structure and the fluorescence contrast was elucidated. The potential of these cyanines as local environmental and structural probes was further demonstrated.

Modulation of the excited-state dynamics at lipid interfaces was illustrated with artificial photosystems made of four octameric units which self-assemble into a quaternary twisted array of π-stacks. It was demonstrated that, after photoexcitation and due to preorganisation, a charge separation process takes place within an octameric unit on an ultrafast time scale, in parallel to coherent and incoherent energy transfer. This charge separation process underlies the activity of these artificial photosystems as light-driven transmembrane electron pumps which allow a p*H* gradient to be established over the membrane of a lipid vesicle.

The numerous experimental examples contribute to showing that preorganised environ-ments affect the early excited-state dynamics of suitable chromophores and that femtosecond-resolved fluorescence spectroscopy is a powerful tool to gain insight into the nanoenviron-ment of fluorescent probes in order to obtain local structural information on biomolecules.

Andreas HENNIG

Development of Two Novel Fluorescent Enzyme Assays: Nano-TRF and Supramolecular Tandem Assays

PhD thesis, Jacobs University Bremen, July, 2007
Working place: School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, D-28759 Bremen, Germany
Supervisor: Werner M. Nau

The detection of enzymatic activity is one of the cornerstones of biochemical research in universities as well as in the pharmaceutical and biotechnological industry, which ultimately enables the possibility to modify, control, and utilize enzymes for numerous applications. So far, a relatively large number of enzyme assays have been envisaged and investigated, which has lead to the conclusion that fluorescence-based assays will step-by-step replace other existing methods. However, the flipside of the coin is the synthetic challenge to modify enzyme substrates with sterically demanding fluorescent probes in such a way that the enzyme-substrate recognition is not hampered. As a potential solution, the present work describes the development of two novel fluorescent enzyme assays, which are minimally invasive, but yet as simple and powerful as possible.

The first method introduces a novel fluorescent probe (DBO) for protease and kinase assays for which the term nanosecond time-resolved fluorescence (Nano-TRF) assays has been coined. Nano-TRF assays exploit the extraordinary photophysical and chemical properties of DBO. The exceedingly long fluorescence lifetime allowed the use of time-gated detection to suppress any undesirable short-lived background fluorescence, which presents a major obstacle in pharmaceutical drug discovery. The electron-rich indole group and the phenolic side chain of tryptophan and tyrosine residues served as efficient intrinsic quenchers of the DBO fluorescence by aborted electron and hydrogen atom transfer, respectively. The frequent natural occurrence of tryptophan and tyrosine in protease and kinase substrates remedied the necessity to introduce an additional quencher and simplified assay design compared to the ubiquitous use of fluorescence resonance energy transfer (FRET). Furthermore, it has been demonstrated by mutation studies that DBO is recognized rather as a small hydrophilic residue than as a hydrophobic residue when compared with common fluorescence probes with extended π-surfaces.

The second method presents a novel, general assay principle, which has been termed supramolecular tandem assays. Commonly, the reversible encapsulation of a fluorescent dye by a macrocycle is accompanied by a change in fluorescence owing to its translocation into an environment with different physical or chemical properties, e.g. a different polarity. Upon competitive displacement, the fluorescence properties are restored, which has quite often been utilized for sensing applications. Supramolecular tandem assays for the first time demonstrated that macrocycle and dye can be chosen in such a way that this dynamic system is capable of signalling enzymatic activity without the necessity to synthetically modify the enzyme substrate. This novel concept has so far been applied to two unrelated enzyme classes, namely amino acid decarboxylases, which play major roles in cancer development and inflammatory processes, and arginase, which is involved in asthma and immune response. The lessons learned from optimizing the decarboxylase and arginase assay were further elaborated on by binding and kinetic simulations, which afforded a generalized concept including guidelines for further development of these types of enzyme assays.

Cecilia MENDIVE

Effect of UV(A) light on chemical reactions at the interface metal oxide / aqueous solution

PhD thesis, National University of San Martín, Buenos Aires, Argentina, March, 2007
Working place: Institute for Technical Chemistry, Leibniz Universität Hannover – Callinstrasse 3, D-30167, Hannover, Germany; and National Commission of Atomic Energy, Av. Gral. Paz 1499, 1650, San Martín, Buenos Aires, Argentina.
Supervisor: Prof. Dr. Miguel Blesa, Prof. Dr. Detlef Bahnemann and Prof. Dr. Thomas Bredow

Attenuated Total Reflection – Fourier Transformed Infrared (ATR-FTIR) spectroscopy, Time Resolved Microwave Conductivity (TRMC) measurements and quantum chemical calculations were performed to study the surface changes upon UV(A) illumination of pure anatase, pure rutile and mixed phases nanoparticles in contact with an oxalic acid solution.

The results showed that the total integrated infrared spectral area of adsorbed oxalic acid increases either upon UV(A) irradiation. This phenomenon was explained assuming deaggregation of particle agglomerates. Furthermore, upon UV(A) illumination, the intensity of some IR absorption bands of adsorbed oxalic acid on TiO_2 increased while, at the same time, that one of some others decreased. By means of quantum chemical calculations and Molecular Dynamics simulations, the spectral changes were found to correspond to surface reactions and rearrangements. For anatase, in which the (100) surface was used for all calculations as it was found by means of High Resolution Transmission Electron Microscopy (HRTEM) investigations, to account for the larger portion of the exposed faces in the nanoparticles, four species were found to contribute to the surface speciation: two monoprotonated monodentate species differing in the position of one H atom (***A-C'1*** and ***A-C3***), one deprotonated bidentate species (***A-A4***) and one monoprotonated bidentate species (***A-B6***). Under UV(A) illumination species ***A-C3*** and ***A-B6*** decrease their surface concentration while the concentration of species ***A-C'1*** and ***A-A4*** increase. Species ***A-C'1*** can (i) convert to species ***A-A4*** releasing •OH radicals or a water molecule, (ii) be reduced to an aldehyde form with the oxidation of the nearby surface OH to adsorbed OOH, (iii) undergo photocatalytic degradation releasing one or two CO_2 molecules and adsorbed formic acid, (iv) convert to adsorbed bicarbonate with elimination of CO. Species ***A-C3*** is not found to undergo photocatalytic degradation, but it appears to act as a very efficient electron-hole trap, as observed in the TRMC measurements. Species ***A-A4*** is found to undergo easily photocatalytic degradation yielding two CO_2 molecules; and species ***A-B6*** undergoes direct photocatalytic degradation releasing •OH radicals. For rutile, using the (110) surface in all calculations, three species were found to contribute to the surface speciation: two bidentate species, one monoprotonated (***R-A1***) and one deprotonated (***R-A2***) and one species monodentate and monoprotonated (***R-C'3***). Under UV(A) illumination, the concentration of the species ***R-C'3*** decreases, while those of species ***R-A1*** and ***R-A2*** increase. Species ***R-A1*** undergoes photocatalytic degradation releasing an •OH radical, while species ***R-A2*** converts into two CO_2 molecules. The photoreactions of species ***R-C'3*** are similar to those of species ***A-C'1*** in anatase, thus, it can convert to the bidentate species ***R-A2*** with the elimination of a water molecule, reduced to an aldehyde form with the oxidation of a neighbour adsorbed OH group into an adsorbed OOH radical and directly converted into one or two CO_2.

Maria Carmen MORANT-MIÑANA

Regio- and stereodifferentiantion in processes photosensitised by aromatic compounds

PhD thesis, Universitat de València, 2nd November, 2007
Working place: Institut de Ciència Molecular (ICmol), Paterna (València)
46980 Polígon de la Coma, s/n, Spain
Supervisor: Julia Pérez-Prieto; Raquel E. Galian

Previous studies performed to gain insight into the chemical nature of the photoproducts that lead to the photoallergic side effects of non-steroidal anti-inflammatory drugs, such as tiaprofenic acid and suprofen, used 2-benzoylthiophene (BT) and indole (InH) and phenol (PhOH) as model substrates. These studies have demonstrated that InH is not the best model to investigate the nature of Trp modification in proteins, since the isolated photoproducts showed InH radicals had coupled through the 3-position, which is not available in the amino acid moiety. Concerning the mechanism of the interaction between InH or PhOH and BT, theoretical calculations (DFT) support the involvement of encounter complexes.

Therefore, one of the objectives of this thesis was to use models closer to the drugs and the protein, i.e. tiaprofenic acid and suprofen esters and indoles substituted in C-3, to obtain information into the nature of the species involved in the covalent incorporation of the drugs to the proteins. Time-resolved studies (laser flash photolysis) showed that irradiation of BT derivatives in the presence of 3-methylindole derivatives generates not only ketyl and indolyl radicals but also skatolyl radicals. Isolation and characterisation of the photoproducts agreed with those studies. The generation of skatolyl radicals by drug photosensitization of 3-alkylindoles is of biological relevance.

On the other hand, the involvement of BT-InH exciplexes was clearly established by using both enantiomers of a chiral BT and chiral quenchers (Tyr and Trp derivatives). Determination of the pre-equilibrium constants (K_{EC}) and the intrinsic decay rate constants (k_d)

for each diastereomeric pair evidenced a significant stereodifferentiation in both steps of the quenching process, which depends on the solvent properties.

The experimental detection of intermolecular BT-indole exciplexes led us to study the potential of intermolecular analogues as triplet photosensitisers. Studies performed using BT-InH bichromophoric compounds provided evidence for the occurrence of triplet-triplet energy transfer from BT-In exciplexes to napthalenes (NP) with a remarkable stereodifferentiation. Interestingly, chiral recognition was also observed in the decay of the generated NP triplets (^{3}NP*) even in those cases where the photosensitiser does not have a stereocenter close to the ketone. This is very interesting taking into account the lack of influence of InH in the quenching of ^{3}NP*. The enantiodifferentiation factor in the decay of ^{3}NP* induced by a bichromophoric compound without chirality in the ketone moiety was found to depend on the temperature. The observation of a switching of enantiodifferentiation with the temperature and a higher recognition at elevated temperatures could be attributed to entropy contribution.

Finally, NP-BT triplet exciplexes were applied for the photosensitized decarboxylation of a NP derivative such as naproxen. It was found that BT plays a dual role: triplet photosensitiser and catalyst. The role of the oxygen is very important to avoid photocatalyst degradation. This strategy has resulted in a new method for naphthylacetic acids decarboxylation.

Melinda NORONHA

Time resolved fluorescence of tyrosine residues: A new tool to characterize protein conformational changes

PhD thesis, Universidade Nova de Lisboa, March, 2007
Working place: Instituto de Tecnologia Química e Biológica,
Apt 127, 2780 Oeiras, Portugal
Supervisors: António Maçanita, Helena Santos and D. Alastair Smith

The use of time-resolved fluorescence spectroscopy (TRFS) to study protein unfolding is complicated by the difficulty of interpreting multi-exponential fluorescence decays, not just in proteins but also in simple peptide systems. The aim of the present study is to evaluate the possibility of using the fluorescence lifetimes and the corresponding pre-exponential coefficients of intrinsic chromophores of a protein, located in different regions of the protein, to probe and report on changes that occur in these specific regions.

The work focuses specifically on the use of tyrosine as the fluorescent probe. Thus, a detailed and systematic characterization of the photophysics of tyrosine is carried out for the model compound, N-acetyltyrosinamide, followed by the application of this information to a protein with a single tyrosine residue, ubiquitin and then to two proteins with multiple tyrosine residues: cytochrome c" (four tyrosine residues) and ribonuclease A (six tyrosine residues).

The study of N-acetyltyrosinamide (NAYA) fluorescence in a series of solvents (including dioxane-water mixtures to mimic the local environment of buried and exposed tyrosine residues in a protein) showed that the double-exponential decays observed for NAYA in highly polar solvents are the result of excited-state electron transfer from the cresol moiety to the backbone carbonyl group. A kinetic model that explains the change from single to double-exponential decays and that can rationalize the occurrence of this change in a protein is presented.

From the observed multi-exponential fluorescence decays of ubiquitin (UBQ) at pH 1.5, the mole fractions of folded and unfolded UBQ, and hence the unfolding equilibrium constant (K_U), could be directly determined as a function of temperature (without having to resort to thermodynamic measurements). The weakness of the tyrosine fluorescence of UBQ at pH ~7 was shown to be due to excited-state proton transfer to a nearby ionized amino acid, glutamate-51 and it was possible to detect excited-state tyrosinate at physiological pH in UBQ.

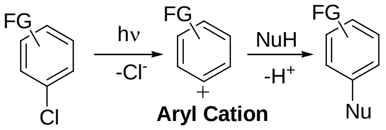
Finally, we show that, even for proteins with multiple tyrosine residues such as cytochrome c" and ribonuclease A, unfolding of the protein can be studied by TRFS by discriminating between the fluorescences of the multiple tyrosine residues. In the case of cytochrome c”, the fluorescence of each of the four tyrosine residues is controlled by dipole-dipole energy transfer from the tyrosine to the heme group. Modification of the tyrosine-heme distances as a result of conformational changes of the protein affects the individual fluorescence decays, making it possible to extract information on the nature of the alterations that occur in the four distinct regions of the protein around the tyrosines. For ribonuclease A, the fluorescence of five of the six tyrosine residues is influenced by short-range excited-state electron transfer from tyrosine to nearby disulfide bridges, permitting the use of TRFS to probe the unfolding/folding of ribonuclease A at six different loci of the protein.

Stefano PROTTI

Photoinduced Arylation Processes

PhD thesis, University of Pavia, January, 2007
Working place: Laboratory of Photochemystry, Department of Organic Chemistry
27035 Pavia, Italy
Supervisor: Prof. Maurizio Fagnoni

The direct formation of an aryl-carbon bond represents a significant synthetic target in organic chemistry. In the last decades several research groups have developed novel metal (especially Palladium or Nickel) catalyzed arylation procedures for the synthesis of biphenyls, phenylacetylenes, styrenes and other important organic molecules. Recently our research group has demonstrated that an actual S_N1 reaction can be accomplished by the metal-free photogeneration (from a phenyl chloride) of a phenyl cation followed by the reaction with π nucleophiles (e.g. alkenes, or (hetero)aromatic derivatives).



NuH = Alkenes, (Hetero)aromatics

In the present work, in order to widen the application of this photo-S_N1 reaction, we first decided to enlarge the scope of the reaction by exploring further aromatic precursors of aryl cations. We have firstly demonstrated that phenyl cations can be also produced by photoinduced heterolysis of aryl-oxygen bond. Irradiation in polar or protic solvents of electron-rich aryl esters, (such as methoxy and amino arylsulfonates or aryl diethyl phosphates), likewise generated phenyl cations, that were exloited in the synthesis of biphenyls and allyl aromatics in almost quantitative yields.

Moreover, a new method was proposed for the synthesis of arylacetylenes based on the reaction of aryl cations with (terminal) alkynes (e.g. 1-hexyne, ethynyltrimethylsilane and trimethylsilylpropyne). Good to excellent yields were obtained starting from an aromatic halide or ester in 2,2,2-trifluoroethanol in the presence of a base (triethylamine). This method could be considered as a photochemical alternative to the Sonogashira cross-coupling procedure, which avoided the use of Pd catalysis and Cu salts because activation of aromatic substrates was promoted by light absorption.

Aryl cations were likewise employed in the synthesis of an important class of compounds viz. γ-benzyl and δ-phenyl lactones. Our synthetic proposal consisted in the photochemical reaction of electron-rich aryl chlorides or esters with ω-unsaturated carboxylic acids, in a acetonitrile/water 5:1 mixture as the solvent. The reaction was both regioselective and diastereoselective, when a non terminal alkenoic acid was used. Under the same conditions, when using ω-alkenols in place of alkenoic acids, phenyl(benzyl) tetrahydrofurans were obtained.

Christian SCHÄFER

Photoswitchable Resorcin[4]arenes

PhD thesis, Universität Bielefeld, July, 2007
Working place: Organische Chemie I, Universität Bielefeld, Universitätsstr. 25,
33615 Bielefeld, Germany
Supervisor: Jochen Mattay

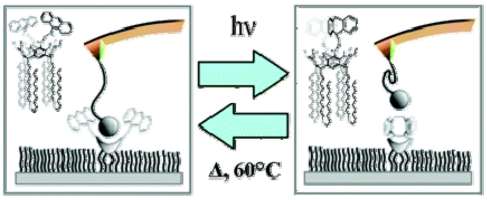
The host-guest properties of resorcin[4]arenes have made these species of the calixarene family an interesting and still intriguing kind of supramolecules. The combination of resorcin[4]arenes with two anthracene moieties on opposite sides at the upper rim provided control of the hosting ability of the resorcin[4]arene through an intramolecular reversible [4+4] cycloaddition of the anthracenes.

The synthesis of various molecules of this kind was accomplished and the photochromic properties were investigated in solution, in the gas phase and on surface.

Affinity Studies in Solution: In solution, we found one species to be able to build a stable (at room temperature) intramolecular anthracene dimer upon irradiation with near UV light. The back reaction to the open form occurred upon heating (to about 60°C). Other compounds reopened immediately after irradiation and some decomposed upon irradiation. The metastable dimers could be stabilized using lower temperatures during and after irradiation or - in one case - through addition of a sodium salt prior to irradiation.

Affinity Studies in the Gas Phase: The gas phase experiments focused on the photoswitchable resorcin[4]arene, which forms a stable intramolecular dimer. Both states of the molecule were introduced and isolated in the ICR cell of a FT-ICR mass spectrometer, in each case as a complex with a specific ammonium ion. After isolation, different gaseous amines were introduced into the ICR chamber and the exchange of guests - for example ammonium versus ethylammonium - was recorded time-dependent to determine the reaction rates. To verify the results, two resorcin[4]arenes with similar structures (except for the anthracenes) were built and investigated by the same method and quantum chemical calculations were performed to underline the results.

Single Molecule Experiments on Surface: The photoswitchable resorcin[4]arene was also modified at the lower rim to build self assembled monolayers (SAMs) on gold. The monolayer was then analyzed with atomic force microscopy (AFM). The tip of the AFM-cantilever had an ammonium-guest attached, which would interact with the open form of the photoswitch. We indeed succeeded in measuring a single molecule interaction force of ~100 pN for the open system. When we irradiated the monolayer and closed the host, the interaction could not be measured any more, whereas upon heating the SAM to about 60 °C, the interaction force was again observed and we hence completed one cycle of photoswitching on a gold surface.



Liana SILVA

Nystatin and Ceramide Interaction with Multicomponent Model Membranes: Relating Membrane Biophysics with Antibiotic Action And Apoptosis

PhD thesis, Technical University of Lisbon, November, 2006
Working place: Centro Química Física Molecular, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
Supervisor: Manuel Prieto

The biophysical properties of membranes and the interaction among their constituent lipids mediate the action of exogenous molecules and govern several biological processes, namely through the formation of membrane domains. To gain further knowledge on this subject, biophysical studies were performed in multicomponent lipid bilayers. Fluorescence spectroscopy, both steady-state and time-resolved, complemented with other biophysical techniques, was used to study the effect of i) sterol type and content in the mechanism of action of the polyene antibiotic nystatin and ii) the sphingolipid ceramide in the properties of fluid membranes. Nystatin ability in permeabilizing lipid vesicles depends primarily on the presence of sterols and on antibiotic concentration in the lipid bilayer, but also on sterol type and relative content, being more effective towards ergosterol-containing vesicles. It is proposed that the architecture of the pores formed is different, depending on the sterol present in the membrane. Concerning ceramide, this sphingolipid strongly changes morphology, biophysical properties, and lipid lateral organization in fluid membranes in a manner dependent on lipid composition, promoting, e.g., an increase in the acyl chain order, gel-fluid phase separation and the formation of a highly-ordered ceramide-rich gel that is abolished by high cholesterol content in raft model membranes.

Serena SILVI

Artificial Molecular Machines

PhD thesis, Università di Bologna , May 2006
Working place: Laboratorio di Fotochimica e Chimica Supramolecolare, Dipartimento di Chimica "G. Ciamician", via Selmi 2
40126 Bologna, Italy
Supervisor: Alberto Credi

Molecular machines are assemblies of molecular components designed to perform a mechanical movement by consuming some form of energy. The molecular machines presented in this thesis are constructed on a class of chemical compounds called pseudorotaxanes and rotaxanes, which can perform rotatory and/or linear motions.

Many features of molecular machines are in common to those of macroscopic machines. For example they need energy to operate: the energy can be chemical, electrochemical or photochemical. Moreover in order to control and monitor the device operation, the rearrangements of the component parts should cause readable changes in some chemical or physical properties of the system. In this regard photochemical and electrochemical techniques are very useful, because photons and electrons are both valuable inputs and outputs. Photochemical and electrochemical stimuli are clean and easy to switch on and off; moreover the time period required to read the state of the system is an important parameter for molecular devices whose operation is based on metastable states. From this point of view, spectroscopic techniques offer unparalleled performances, allowing processes to be studied down to the femtoseconds time scale.

All the supramolecular systems and corresponding molecular components presented in the thesis have been studied in solution. The systems have been characterized using the following experimental techniques: absorption and emission spectroscopy, luminescence lifetime measurements, electrochemistry and stopped-flow experiments. The results of this work arise from fruitful collaborations with several research groups.

In collaboration with the group of Prof. Loeb at the University of Windsor (Canada), we characterized a series of heteroleptic Ru(II) rotaxane complexes, which show favourable photophysical properties and structural advantages.

In collaboration with the group of Prof. Stoddart at the University of California Los Angeles we designed, constructed and operated a triply-threaded, two-components molecular machine that behaves like a nanometre-scale elevator.

During a research period of six months at the University of Miami, in the laboratory of Prof. Kaifer, we designed and studied a pH-driven pseudorotaxane based on cucurbit[7]uril that works in aqueous solution.

This research field is new and it is growing quickly: indeed molecular machines represent an important contribution to the development of nanoscience and nanotechnology. In this work we showed some of the progresses of this new research field: thank to the progresses of organic chemistry some of these systems are structurally extremely complex and sometimes aesthetically appealing, or in other cases their value resides in their simplicity. Many potentialities and possible applications of molecular machines probably are not yet even imagined. This new, still unexplored, field leaves space to fantasy and imagination.

Ignacio VAYÁ

Excited states of the non-steroidal antiinflammatory drug flurbiprofen as probes for the interaction with proteins

PhD thesis, Universidad Politécnica de Valencia, November, 2007.
Working place: Departamento de Química-Instituto de Tecnología Química UPV-CSIC. Camino de Vera s/n, 46022, Valencia, Spain.
Supervisor: Miguel Angel Miranda Alonso and M. Consuelo Jiménez Molero.

Serum albumins are proteins very abundant in the organism. One of their main physiological functions is to act as a vehicle for different endogenous and exogenous agents (including drugs) through the blood-stream.

Binding of drugs to SA in biological systems is a key process that can modulate a number of properties of the carried agent, such as increased solubility in plasma, decreased toxicity, etc.; hence, binding is essential for understanding biodistribution, metabolism, elimination or pharmacological effect of drugs in the body. Several techniques have been used to investigate drug-protein binding processes. The aim of this work has been to develop alternative methodologies in order to get further insight into the relevant interactions taking place between the non-steroidal antiinflammatory drug flurbiprofen (FBP) and the human and bovine serum albumins (HSA and BSA). For this purpose, the transient species generated by irradiation were used as probes to study the nature of these interactions, as their properties serve as quantitative parameters sensitive to the microenvironment. Thus, fluorescence and laser flash photolysis techniques were used.

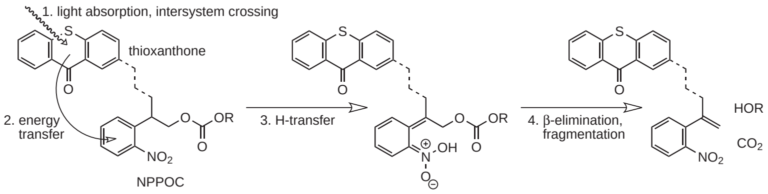
First, the first excited states of FBP were fully characterised and several model dyads containing FBP and tyrosine or tryptophan (the main aminoacids involved in the interaction of the drug in the active site of the protein) were studied in order to obtain information about the operating mechanisms in the excited state interactions. The results showed that singlet excited state of FBP was highly sensitive to the drug-amino acid interaction, which was stereoselective. For further progress in the understanding of drug/protein interactions, intermolecular drug/SA systems were studied. In these cases, the first triplet excited state of FBP was highly sensitive to the environment provided by the binding sites of the protein. A relevant observation was that triplet lifetimes of the drug were longer in the presence of protein. This can be attributed to a slower deactivation of the excited states inside the protein binding sites, where an exceptional microenvironment protecting the triplet excited state from attack by a second drug molecule, oxygen or other reagents is provided. Regression analysis of the decay kinetics of the transient absorption spectra corresponding to the triplet-triplet absorption provided precise information on the number of binding sites and their degree of occupancy. Moreover, the assignment of the drug bound in site I and site II in SA was confirmed by displacement of the drug by selective site II probes. A remarkable stereodifferentiation of the triplet lifetimes of the drug within the protein was observed, in addition to a moderated stereodifferentiation in the occupation level of the two binding sites of the SA. Finally, LFP technique provided information about the binding degree of FBP in the presence of different host biomolecules simultaneously.

Dominik WÖLL

New photolabile protecting groups with intramolecular sensitization – Synthesis, photokinetic characterization and application for DNA chip synthesis

PhD thesis, Universität Konstanz, März, 2006
Working place: AG Steiner, Fachbereich Chemie,
Universität Konstanz, Universitätsstraße 10, 78457
Konstanz, Germany
Supervisor: Prof. Dr. Ulrich Steiner

For an efficient synthesis of high-density DNA chips, photolabile protecting groups with high light sensitivity, high nucleoside yields and a minimum of side reactions are imperative.[1] The NPPOC protecting group complies well with the latter two requirements, but has low absorption coefficients < 300 $M^{-1}cm^{-1}$ at 366 nm and 405 nm, the mercury lines most suitable for irradiation. Thus, despite a good quantum yield of 0.4 the light sensitivity of NPPOC is low. As has been successfully demonstrated in homogeneous solution and on chips,[2] indirect excitation through energy transfer from triplet sensitizers such as thioxanthone represents an elegant possibility to overcome this problem. In this thesis, a considerable step forward was taken by designing a series of photolabile protecting groups wherein NPPOC is covalently linked to thioxanthone as an intramolecular antenna. The photochemical functioning of these dyads has been characterized in detail. Intramolecular energy transfer is generally fast but depends on the length and structure of the linker. For short aliphatic linkers, a surprising discovery was made. Although the S_1 state of NPPOC is significantly higher than the S_1 state of thioxanthone, efficient singlet quenching of the sensitizer with a concomitant efficient photocleavage of NPPOC occurs. This observation led to the discovery of a fast $S_1(\pi\pi^*) \rightleftarrows T_2(n\pi^*)$ equilibrium in thioxanthone.[4] The new generation of photolabile protecting groups synthesized in this work exhibits strong enhancement of light sensitivity. Compared to the parent NPPOC group, the light sensitivity could be increased by up to a factor of 20 at 366 nm and 140 at 405 nm. Some of the new compounds show little side reactions and have been successfully tested under the conditions of automated DNA chip synthesis.



[1] M. C. Pirrung, *Angew. Chem. Int. Ed.* **2002**, *41*, 1276-1289.

[2] D. Wöll, S. Walbert, K.-P. Stengele, T. J. Albert, T. Richmond, J. Norton, M. Singer, R. D. Green, W. Pfleiderer, U. E. Steiner, *Helv. Chim. Acta* **2004,** 87, 28-45.

[3] D. Wöll, J. Smirnova, W. Pfleiderer, U. E. Steiner, *Angew. Chem. Int. Ed.* **2006**, *45*, 2975-2978.

[4] D. Wöll, S. Laimgruber, M. Galetskaya, J. Smirnova, W. Pfleiderer, B. Heinz, P. Gilch, U. E. Steiner, *J. Am. Chem. Soc.* **2007**, *129*, 12148-12158.

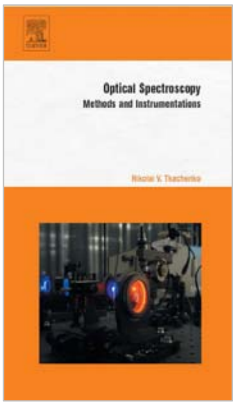
[5] D. Wöll, J. Smirnova, M. Galetskaya, T. Prykota, J. Bühler, K.-P. Stengele, W. Pfleiderer, U. E. Steiner *Chem. Eur. J.* **2008**, *accepted.*

Books

Optical Spectroscopy
Methods and Instrumentations

by Nikolai V. Tkachenko

Elsevier, 2006
ISBN-13: 978-0-444-52126-2, ISBN-10: 0-444-52126-7



Recent developments in lasers, optics and electronics have had a significant impact on modern optical spectroscopic methods and instrumentations. Combining the newest lasers, advanced detectors and other high technology components researchers are able to assemble a spectroscopic instrument with characteristics that were hardly achievable a decade ago. On the other hand the researchers, who are potentially interested in such spectroscopy applications, are experts in the fields of their own professional interest, such as materials science or microbiology, and may have only basic background knowledge in optics and modern laser physics. A single source of information describing different optical spectroscopy techniques in details essential for practical work and suitable for students with non-technical background has been missing. This problem was solved two years ago when the present book was published by Elsevier. The book provides the reader with background knowledge required for qualified research work with modern spectroscopy instruments.

Logically the book can be divided on two parts. The first part, Chapters 1-4, covers a few subjects important for technical implementations of all spectroscopy instruments such as optics, opto-electronics and laser physics. This part of the book is intended to remind readers of the key concepts, important theories, principle values and available tools which are used in spectroscopy applications. One example of such tool is a monochromator, which can be found in almost every spectroscopy device and determines important characteristics of the devices such as spectrum range and resolution.

The second part, Chapters 5-13, is the main part of the book, which is divided according to the types of the optical spectroscopy methods described. Each Chapter starts with a general description of the design principles, and follows by an introduction of the approaches used to estimate the most important features of the instrument, such as spectrum and time resolution, and by discussions of what are applicability ranges for this particular spectroscopy technique. In the final part of each Chapter examples of the instruments and measurements are provided. The order of the Chapters roughly follows the order of inventing different spectroscopy methods and one can see that the important direction in the development of optical spectroscopy instruments was the continuous improvement of the time resolution – from steady state spectroscopy to nanosecond methods, picosecond and finally femtosecond techniques.

Two last topics discussed in the book are polarization (Chapter 14) and analysis of the measurements (Chapter 15). They are important to all spectroscopy techniques and, therefore, were arranged as separated Chapters.

As time passed, a number of mistakes has been discovered in the book. They are listed in the author web-page at http://kemia.me.tut.fi/nick/OptSpec/corrections.html.

Elina Vuorimaa, Lecturer
Tampere University of Technology
Department of Chemistry and Bioengineering

CONFERENCE REPORTS

RSC Photochemistry Group Young Researchers' Meeting
December 6th 2007, Loughborough University, UK

Loughborough University hosted the Young Photochemistry Researchers conference on the 6th of December this year. This conference was organised by the RSC Photochemistry group, headed by Dr David Worrall. The RSC photochemistry group has over 200 members, of which around 50 of these are based overseas, of which people had travelled from as far away as Malaysia to attend. This is the latest photochemistry meeting held in Loughborough which follows in the footsteps of a very successful meeting at the Rutherford Appleton laboratory in December 2004, which enables young PhD research students and lecturers to present their work and discuss it with colleagues researching in the photochemistry field.

Plenary lectures were delivered by Professor Sir Richard Friend FRS of Cambridge University and Professor Robin Perutz of York University on selective ion sensors and photo-induced electron transfer catalysis. Work presented during the day included the control of photochemical properties via isomerisation and via functional group transformations. Another eleven lectures were given by students and lecturers from universities all over Britain.

Nearly 40 posters were displayed overall, displaying work done in institutions within the UK and Ireland, and with many collaborations from overseas universities in Europe, the Far East and the USA. The poster prize was presented to Miss Emma Coyle, from Dublin City University by Dr. David Worrall from the Loughborough University Chemistry Department.

James Fletcher
Nadya Muhammed
Loughborough University

Autumn Meeting of the French Group of Photochemistry (GFP)

Cachan, France, 29th -30th November 2007

Outside in Cachan it was cold, humid, grey and dark, as is not uncommon for a Thursday at the end of November in the region near Paris. At the Autumn Meeting ("*Journées d'Automne 2007*") of the *Groupe Français de Photochimie*, the light was inside. The comfortably warmed lecture room at the *Ecole Normale Supérieure de Cachan* was very well filled with photochemists from laboratories in France and beyond (Belgium, Germany, Switzerland). The spectrum of the nationalities of the participants was even more diverse. This autumn meeting was organized by Edmond Amouyal (Palaiseau) with the help of Isabelle Leray (Cachan) and Jacques Delaire (Cachan).

Newly elected EPA chairperson Dimitra Markovitsi presented the recent evolution of the European Photochemistry Association EPA, both on the pan-European and national levels. Special attention was drawn to the newly created EPA PhD Thesis Prize and the upcoming IUPAC 2008 Photochemistry Symposium in Gothenburg (Sweden). The morning session continued with a presentation by François-Alexandre Miannay (Saclay) on the investigation of cooperative effects in the photophysics of double DNA strands consisting exclusively of guanine-cytosine base pairs using ultrafast spectroscopy and quantum chemical calculations. Johanna Brazard (Paris) gave a detailed account of the primary events in the photocycle of a photophobic micro-organism (Blepharisma japonicum) as seen by sub-picosecond transient absorption spectroscopy of this organism's photoreceptor. Data analysis through Singular Value Decomposition helped in building kinetic models, revealing the existence of reactive and non-reactive forms of the photoreceptor. Fabienne Alary (Toulouse) discussed quantum chemical calculations (of the density functional and time-dependent density functional kinds) of the excited states of $Ru(bpy)_3^{2+}$ and related complexes, in particular giving new insight into the structure and photoreactivity of their metal-centered triplet states.

After the coffee-break, Bastian Noller (Würzburg, Germany) explained how to generate and study the photochemistry of reactive intermediates (carbenes, radicals) in a supersonic jet using pyrolysis, laser excitation and multiphoton ionisation followed by mass-spectrometric (time-of-flight) detection, all in high vacuum. He applied the technique to the investigation photodissociation reactions of 1- and 2-propyl radicals. Ákos Bányász (Saclay) presented work on the very fast nonradiative deactivation of the excited singlet state in various uracil derivatives, which were studied using femtosecond fluorescence upconversion. Patrice Bordat (Pau) showed how to avoid being misguided by fluorimetric artefacts in heavily scattering dye-doped silica powders. Spectral shifts displayed by the encapsulated dyes, frequently interpreted in terms of excitonic coupling, can be entirely attributed to optical artifacts resulting from scattering, as was illustrated by Monte-Carlo simulations of the fluorescence measurements on these materials. The morning session ended with a presentation by Hiroshi Uji-i (Leuven, Belgium) on wide-field fluorescence microscopy of individual fluorescently labeled phospholipase enzymes and fluorescently doped phospholipid bilayers. Seeing individual enzymes eating away on phospholipid membranes seemed a fitting and very interesting prelude to lunch.

The afternoon was reserved for a special session in honor of Roland Bonneau (Bordeaux), whose name will be not unfamiliar to several generations of photochemists, especially those having been or currently involved in transient absorption spectroscopy (or flash photolysis). The session was filled personal recollections, retrospectives and recent work. Edmond Amouyal reminded the audience that Roland Bonneau was in charge of the GFP biannual meetings during the 1985-1992 period. In particular, he co-organized the first Joint Meeting of the Italian and French Photochemistry Groups in La Baume-lès-Aix in October 1989. Jacques Joussot-Dubien (Bordeaux) started with a particularly vivid personal account of his years with Roland Bonneau. With a particularly rich use of the French language, he described how they took advantage of the fabrication in 1968 by the CGE company of the first pulsed laser in France (a Nd^{3+} glass laser whose output was quadrupled to yield very intense nanosecond pulses at 264.5 nm) to perform transient absorption studies on aromatics such as naphthalene and benzene. These studies were the start of a productive enterprise using laser flash photolysis to study the fates of excited molecules. Jacques Joussot-Dubien then explained how he became interested in a different research theme, bioelectromagnetism, stressing the importance of measurement and experimentation to generate knowledge, especially in such publically debated subjects as the effect of strong electromagnetic fields on living organisms. Users of mobile phones can rest assured: no evident dangerous side-effects have been found yet. Jakob Wirz (Basel, Switzerland), a friend and collaborator of Roland Bonneau, presented a fascinating variety of work in photochemistry, ranging from solar energy to the art and artefacts of flash photolysis, photochromism, and recent work on photocleavable groups. This lecture was followed by a contribution from Jean-Claude Rayez (Bordeaux) who shared personal memories about the early days in Bordeaux, and then spoke of the power of transition state theory for the understanding of reaction dynamics. The special session ended with a lecture by Dario Bassani (Bordeaux) who drew attention to the important role that (photo)chemists can play in sustainable development, for example in solar energy conversion. He gave an overview of the control of light-induced processes in a variety of supramolecular assemblies.

The first session of Friday started with a talk by Sophie Le Caer (LCF, CEA-Saclay) on water and proton transfer at the alumina-air interface. The discussion was followed by an intervention of Fabrice Morlet-Savary (Mulhouse) who explained the photodissociation reaction of aromatic ketones. Satchin Soorkia (LFP, CEA-Saclay) was interested in the formation of the radical ZrF. Isabelle Couturier

(Marseille) described the photochemistry of cyanopolyynes involved in interstellar chemistry, while Minh-Huaong Ha-Thi (LFP, CEA-Saclay) related the elaboration of new fluorescent probes to detect heavy metal like Hg^{2+} in organo-aqueous medium.

After the break, the final session was dedicated to Michèle Bolte (Aubière, Clermont-Ferrand university). Jacques Delaire (ENS-Cachan) opened the session. First off, Claire Richard (Aubière) explained how Michèle Bolte realized her PhD in Clermont-Ferrand, and after a post-doc in Boston, came back to their laboratory to deal with two main projects: photochemistry applied to environmental problems and the interaction metal-polymer for holography applications. She finished by describing how humic acids could be potential photosensitizers. Another talk should have been given by Agnès Rivaton (Aubière) to honour Michèle Bolte but she couldn't attend the conference and Michèle Bolte herself gave the speach dealing with holography. The last speaker of the day was Gilles Mailhot (Aubière) who was concerned by the use of iron for environmental applications.

As usual, this meeting was a great success. It was well-organized, all the talks were of very good quality. The subjects covered all the main fields of photophysics and photochemistry at the interface of chemistry, physics and biology. Edmond Amouyal, GFP president, closed the meeting by announcing that the GFP Spring Meeting will be held in Brest, Brittany (France) in May 2008.
One thing people will not forget: the taste of the Pineau des Charentes Roland Bonneau offered Thursday evening and Friday at the end of the meeting!

Martinus H. V. Werts
Chimie et Photonique Moléculaires, UMR 6510 CNRS-Université de Rennes 1, Rennes, France
and **Céline Frochot**
Département de Chimie Physique des Réactions (DCPR), UMR 7630 CNRS-INPL, Groupe ENSIC, Nancy, France

CECP 2008
February 10th to 14th 2008, Bad Hofgastein/Austria

From February 10 to 14, 2008, 113 photochemists from 18 different countries came together to share their results and experiences at the Congress Centre of Bad Hofgastein/Austria. Is was a wonderful atmosphere and all participants really enjoyed the meeting. The scientific organization has been done by the international scientific committee: Dario Bassani, Bordeaux/France, Günther Knör, Linz/Austria, Eric Vauthey, Geneva/ Switzerland, Otto Horváth, Veszprém/Hungary, Kamil Lang, Rez/Czech Republic, Nikita Lukzen, Novosibirsk/Russia, Jochen Mattay, Bielefeld/Germany, and Luca Prodi, Bologna/Italy.

Plenary speakers of **CECP 2008**, from left to right Markovitsi, Horváth, Rau, Baklanov, Desvergne, and Sortino.

From Monday to Wednesday there were two sessions per day with one plenary lecture in each session (6 plenary lectures and an experimental lecture of **Michael Tausch** from Wuppertal/Germany), as well as short talks (26 short talks), and a poster session every evening (64 poster presentations). Plenary lectures have been given by **Attila Horváth**, Veszprém, Hungary on photochemistry of Ru(II)-complexes, **Sven Rau**, Jena, Germany on photocatalytic water splitting, **Alexey Baklanov**, Novosibirsk, Russia on $X\text{-}O_2$, **Jean-Pierre Desvergne**, Bordeaux, France on photochemistry of linear acenes, and **Salvatore Sortino**, Catania, Italy about photoactive thin films and nanoparticles.

In order to keep the scientific level of the meeting on a internationally high one the scientific committee selected 6 plenary lectures (out of 19 suggestions) and 26 (out of 41 applications) short talks. All poster applications were accepted after checking by the local committee. All travel grant applications (altogether 20) could be accepted for funding. Additional funding from DFG (German Science Foundation via Jochen Mattay) for invited speakers and German students is also gratefully acknowledged. The local organizing committee has been formed by: Stephan Landgraf (local coordinator from EPA Austria), Christine Onitsch (conference secretary), Anne-Marie Kelterer, Sabine Richert, Asim Mansha, and Martin Knapp. Additional help from Heidi Schmitt is also gratefully acknowledged. The variety of different accommodations is available in Bad Hofgastein from private rooms up to hotels with a high comfort. Even during high season rooms are available in appropriate number if booked early enough. Contact person for accommodation: Monika Kendelbacher, tourist office. Official web site of the meeting: www.ptc.tugraz.at/gastein

The key idea of the CECP meeting is to bring together young and experienced photochemists from all photochemical fields. Therefore everything was done to remove all hindrance to join the meeting. Additionally the evening should be undisturbed by the dinner. So four evening buffets were organized for all participants. The costs were included in the conference fee. So for students the conference itself has been free of charge. Young researchers up to 4 years after PhD and all attendees from Eastern European countries could join for a reduced fee, too. The system behind this could be seen in the budget plan of the meeting (Fig. 1). For **CECP 2010** held in February, 2010, in Bad Hofgastein a small increase of the fees has to be accepted to compensate inflation.

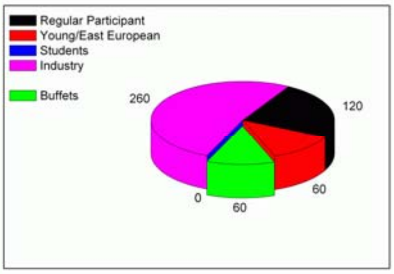


Fig. 1: Budget plan of CECP 2008 (in €) including early paying bonus.

The location of the Conference Centre of Bad Hofgastein allows a perfect access to physical activities during the afternoon break. Downhill and cross-country skiing, as well as the thermal bath and spa, offer a variety of possibilities to enjoy the region or to relax. Together with the scientific program an ideal combination is present at this place.

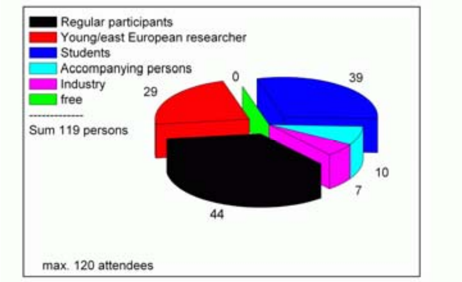


Fig. 2: Registered attendees and accompanying persons.

Finally 119 persons registered for the meeting till the beginning of the conference. 33 % were students (PhD not completed), 37 % were regular participants including plenary lecturers, scientific committee and the local coordinator, 18 % were attendees from Eastern Europe, and 7 % young researchers (from the rest of Europe). The latter two groups only had to pay the reduced fee. The following two diagrams show the distribution of the participants of **CECP 2008** (Fig. 2,3).

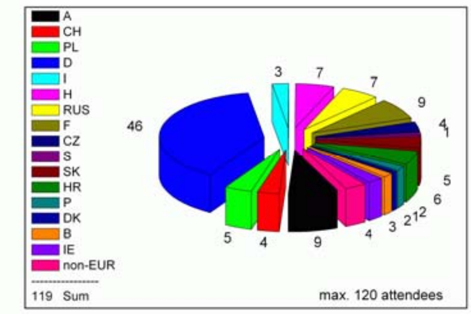


Fig. 3: Registered attendees sorted by country. Finally 113 participants arrived Bad Hofgastein.

The income of **CECP 2008** (Fig. 4) is split into the conference fees of regular participants (39 %), from Eastern Europe (14 %), young researchers (5 %), and students (11 %). Additional funding could be obtained by the Swiss Chemical Society (10 %, via n kind) from industry could also been achieved by the local coordinator (16 %). The rest to 100 % came from accompanying persons and reserves from 2006.

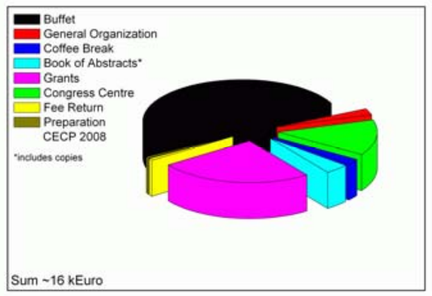


Fig. 4: Income of CECP 2008.

The expenses of **CECP 2008** (Fig. 5) were dominated by the evening buffets (51 %, real costs: 16.36 € per person and day). The conference centre with everything included, like rooms, poster boards, beamer, technician, etc., could be rented for a moderate price (14 %). The costs for general organization could be kept low (2 %). Parts of it, such as coffee pots and trolley, could be used from the **CECP 2006** meeting and can be reapplied for a future meetings as well. The rest of this part was travel costs during preparation of the meeting and material for the poster sessions. Due to hard work of the local team in Bad Hofgastein the costs for the coffee breaks was exceptionally low (2 %, real costs: 0.92 € per person and day). Coffee, tea, and other soft drinks have been offered during the whole meeting. All costs for the book of abstracts (125 pieces), other copies and name tags summed up to 4 %. Less than 1 % has been returned to attendees not able to join the meeting due to illness (full return). 25 % could be used for

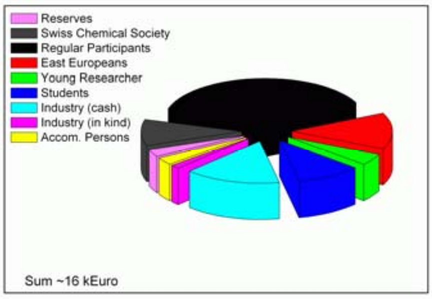


Fig. 5: Expenses of CECP 2008.

travel grants for students, young researchers and persons form Eastern Europeans.

All travel grant applications have been accepted by the local coordinator. 20 attendees have been supported only this way (additional grants for Swiss and German participants have been given by the Swiss Chemical Society and the DFG, but not via the local coordinator). Statistics: A: 3, PL :3, RUS: 5, IE: 3, HR: 3, Egypt: 1, Georgia: 2.

CECP 2008 Awards for Young Scientists

Additionally there are two prices for young scientists to encourage them to present their best results at the CECP meeting. All oral and poster presentations have been evaluated by the international scientific committee. Both prices have been awarded by Axel Griesbeck, Cologne at the end of the meeting prior to the conference dinner on Wednesday.

CECP 2008 Award for best oral presentation: (O10), **David Bailey**, Bremen/D
"Supramolecular Tandem Assays: Monitoring Enzymatic Reactions Using Macrocycle- Encapsulated Fluorescent Dyes"
CECP 2008 Award for best poster presentation: (P10), **Katja Drexler**, Konstanz/D
"Photokinetics of photolabile protecting groups on gold surfaces studied by XPS and SPR"

INVITATIONS

XXII IUPAC Symposium on Photochemistry July 28th to August 1st, 2008, Gothenburg, Sweden

Correspondence

More information, as it becomes available, will be posted on the Symposium website:

http://photoscience.la.asu.edu/Goteborg2008/

Correspondence should be sent to:

Professor Devens Gust
IUPAC Symposium on Photochemistry
Department of Chemistry and Biochemistry
Arizona State University
Tempe, AZ 85287-1604 USA

E-mail: gust@asu.edu

Cover photo copyright 2004 cambridge2000.com

International Scientific Committee

Edmond Amouyal (France)
Tatsuo Arai (Japan)
Mark Van der Auweraer (Belgium)
Josef Baader (Brazil)
Andrew Beeby (UK)
Cornelia Bohne (Canada)
A.M. "Fred" Brouwer (The Netherlands)
Hugh Burrows (Portugal)
Ken Ghiggino (Australia)
Nina Gritsan (Russia)
Miklós Kubinyi (Hungary)
Jochen Mattay (Germany)
Julia Pérez-Prieto (Spain)
Franco Scandola (Italy)
He Tian (China)
John Toscano (USA)
Jakob Wirz (Switzerland)

Local Organizing Committee

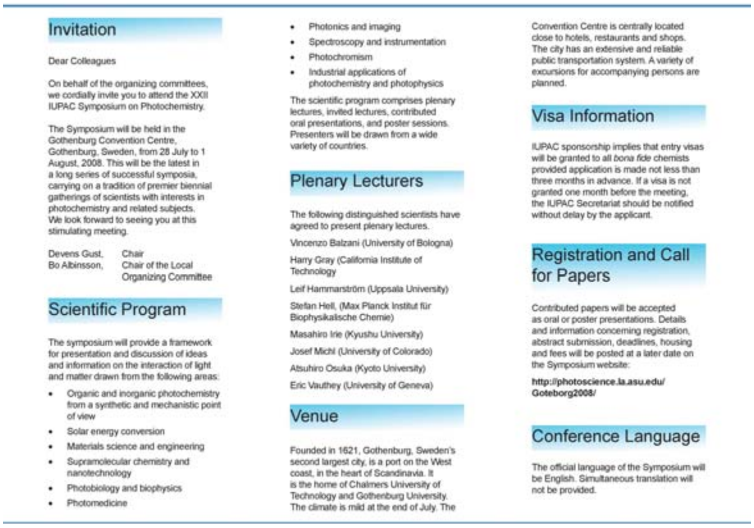
Bo Albinsson (Chalmers University)
Joakim Andréasson (Chalmers University)
Leif Hammarström (Uppsala University)
Lennart B-Å Johansson (Umeå University)
Villy Sundström (Lund University)

XXII IUPAC SYMPOSIUM ON PHOTOCHEMISTRY 2 0 0 8

First Announcement

XXII^nd IUPAC SYMPOSIUM ON PHOTOCHEMISTRY

GOTHENBURG, SWEDEN
JULY 28 — AUGUST 1, 2008



Invitation

Dear Colleagues

On behalf of the organizing committees, we cordially invite you to attend the XXII IUPAC Symposium on Photochemistry.

The Symposium will be held in the Gothenburg Convention Centre, Gothenburg, Sweden, from 28 July to 1 August, 2008. This will be the latest in a long series of successful symposia, carrying on a tradition of premier biennial gatherings of scientists with interests in photochemistry and related subjects. We look forward to seeing you at this stimulating meeting.

Devens Gust,	Chair
Bo Albinsson,	Chair of the Local Organizing Committee

Scientific Program

The symposium will provide a framework for presentation and discussion of ideas and information on the interaction of light and matter drawn from the following areas:

- Organic and inorganic photochemistry from a synthetic and mechanistic point of view
- Solar energy conversion
- Materials science and engineering
- Supramolecular chemistry and nanotechnology
- Photobiology and biophysics
- Photomedicine
- Photonics and imaging
- Spectroscopy and instrumentation
- Photochromism
- Industrial applications of photochemistry and photophysics

The scientific program comprises plenary lectures, invited lectures, contributed oral presentations, and poster sessions. Presenters will be drawn from a wide variety of countries.

Plenary Lecturers

The following distinguished scientists have agreed to present plenary lectures.

Vincenzo Balzani (University of Bologna)

Harry Gray (California Institute of Technology

Leif Hammarström (Uppsala University)

Stefan Hell, (Max Planck Institut für Biophysikalische Chemie)

Masahiro Irie (Kyushu University)

Josef Michl (University of Colorado)

Atsuhiro Osuka (Kyoto University)

Eric Vauthey (University of Geneva)

Venue

Founded in 1621, Gothenburg, Sweden's second largest city, is a port on the West coast, in the heart of Scandinavia. It is the home of Chalmers University of Technology and Gothenburg University. The climate is mild at the end of July. The Convention Centre is centrally located close to hotels, restaurants and shops. The city has an extensive and reliable public transportation system. A variety of excursions for accompanying persons are planned.

Visa Information

IUPAC sponsorship implies that entry visas will be granted to all *bona fide* chemists provided application is made not less than three months in advance. If a visa is not granted one month before the meeting, the IUPAC Secretariat should be notified without delay by the applicant.

Registration and Call for Papers

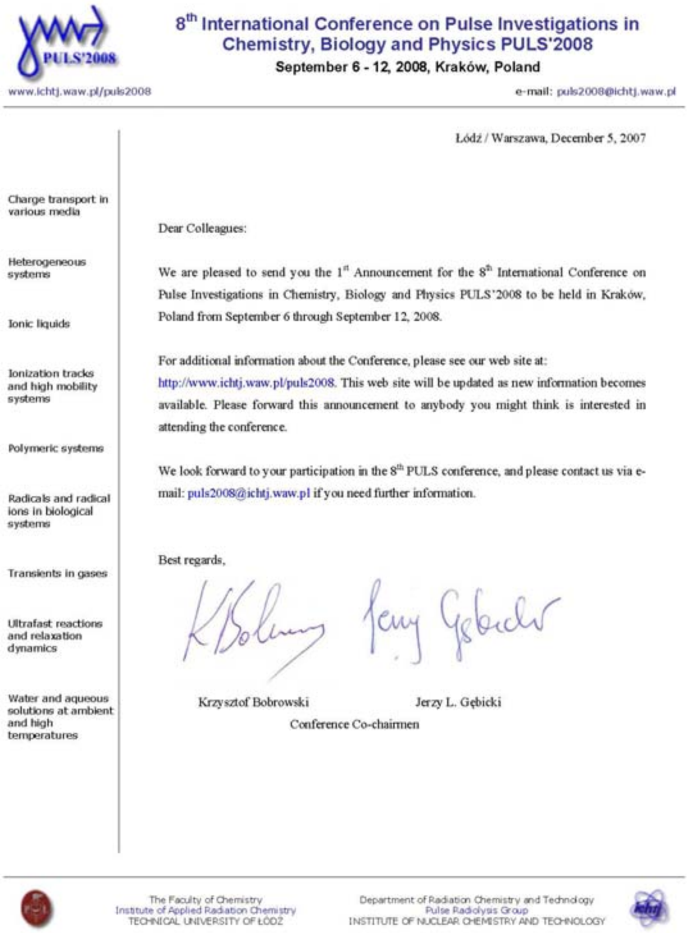
Contributed papers will be accepted as oral or poster presentations. Details and information concerning registration, abstract submission, deadlines, housing and fees will be posted at a later date on the Symposium website:

http://photoscience.la.asu.edu/Goteborg2008/

Conference Language

The official language of the Symposium will be English. Simultaneous translation will not be provided.

8th International Conference on Pulse Investigations in Chemistry, Biology and Physics PULS'2008, September 6th to 12th, 2008, Kraków, Poland.



PULS'2008

8th International Conference on Pulse Investigations in Chemistry, Biology and Physics PULS'2008
September 6 - 12, 2008, Kraków, Poland

www.ichtj.waw.pl/puls2008
e-mail: puls2008@ichtj.waw.pl

- Charge transport in various media
- Heterogeneous systems
- Ionic liquids
- Ionization tracks and high mobility systems
- Polymeric systems
- Radicals and radical ions in biological systems
- Transients in gases
- Ultrafast reactions and relaxation dynamics
- Water and aqueous solutions at ambient and high temperatures

Łódź / Warszawa, December 5, 2007

Dear Colleagues:

We are pleased to send you the 1st Announcement for the 8th International Conference on Pulse Investigations in Chemistry, Biology and Physics PULS'2008 to be held in Kraków, Poland from September 6 through September 12, 2008.

For additional information about the Conference, please see our web site at: http://www.ichtj.waw.pl/puls2008. This web site will be updated as new information becomes available. Please forward this announcement to anybody you might think is interested in attending the conference.

We look forward to your participation in the 8th PULS conference, and please contact us via e-mail: puls2008@ichtj.waw.pl if you need further information.

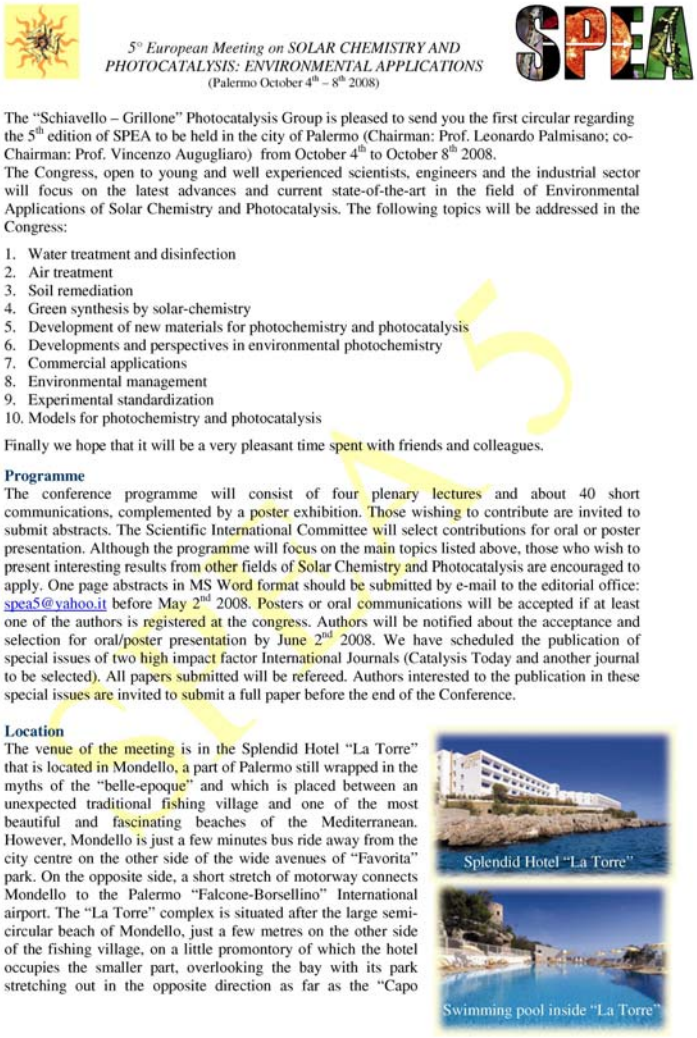
Best regards,

Krzysztof Bobrowski Jerzy L. Gębicki
Conference Co-chairmen

The Faculty of Chemistry
Institute of Applied Radiation Chemistry
TECHNICAL UNIVERSITY OF ŁÓDZ

Department of Radiation Chemistry and Technology
Pulse Radiolysis Group
INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY

5th European Meeting on Solar Chemistry and Environmental Applications SPEA 5, October 4th to 8th, 2008, Palermo, Italy



5° European Meeting on SOLAR CHEMISTRY AND PHOTOCATALYSIS: ENVIRONMENTAL APPLICATIONS
(Palermo October 4th – 8th 2008)

The "Schiavello – Grillone" Photocatalysis Group is pleased to send you the first circular regarding the 5th edition of SPEA to be held in the city of Palermo (Chairman: Prof. Leonardo Palmisano; co-Chairman: Prof. Vincenzo Augugliaro) from October 4th to October 8th 2008.
The Congress, open to young and well experienced scientists, engineers and the industrial sector will focus on the latest advances and current state-of-the-art in the field of Environmental Applications of Solar Chemistry and Photocatalysis. The following topics will be addressed in the Congress:

1. Water treatment and disinfection
2. Air treatment
3. Soil remediation
4. Green synthesis by solar-chemistry
5. Development of new materials for photochemistry and photocatalysis
6. Developments and perspectives in environmental photochemistry
7. Commercial applications
8. Environmental management
9. Experimental standardization
10. Models for photochemistry and photocatalysis

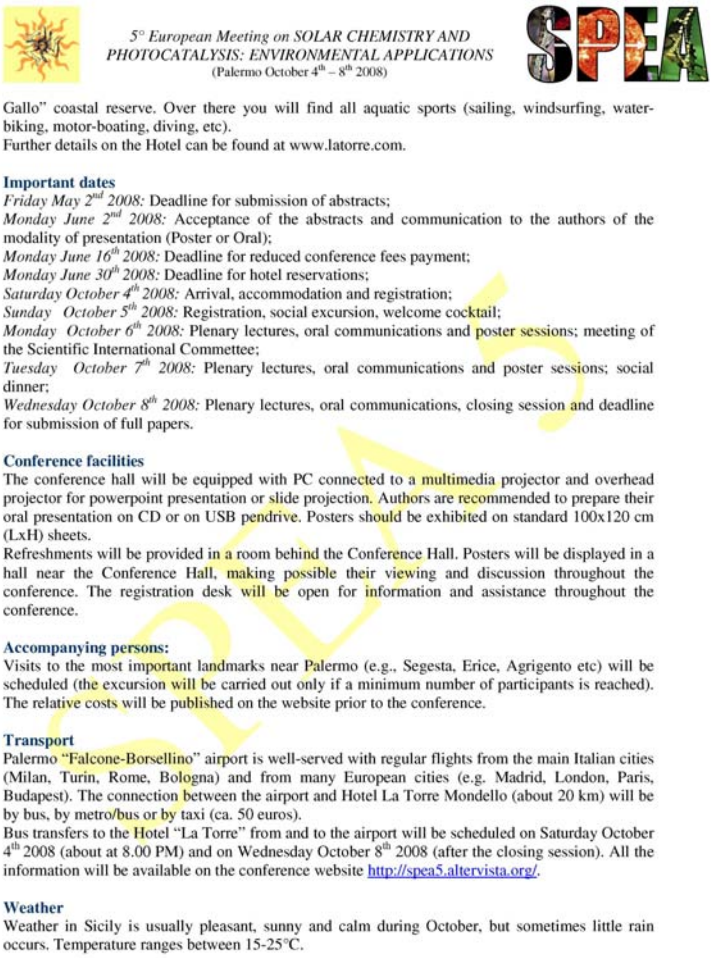
Finally we hope that it will be a very pleasant time spent with friends and colleagues.

Programme
The conference programme will consist of four plenary lectures and about 40 short communications, complemented by a poster exhibition. Those wishing to contribute are invited to submit abstracts. The Scientific International Committee will select contributions for oral or poster presentation. Although the programme will focus on the main topics listed above, those who wish to present interesting results from other fields of Solar Chemistry and Photocatalysis are encouraged to apply. One page abstracts in MS Word format should be submitted by e-mail to the editorial office: spea5@yahoo.it before May 2nd 2008. Posters or oral communications will be accepted if at least one of the authors is registered at the congress. Authors will be notified about the acceptance and selection for oral/poster presentation by June 2nd 2008. We have scheduled the publication of special issues of two high impact factor International Journals (Catalysis Today and another journal to be selected). All papers submitted will be refereed. Authors interested to the publication in these special issues are invited to submit a full paper before the end of the Conference.

Location
The venue of the meeting is in the Splendid Hotel "La Torre" that is located in Mondello, a part of Palermo still wrapped in the myths of the "belle-epoque" and which is placed between an unexpected traditional fishing village and one of the most beautiful and fascinating beaches of the Mediterranean. However, Mondello is just a few minutes bus ride away from the city centre on the other side of the wide avenues of "Favorita" park. On the opposite side, a short stretch of motorway connects Mondello to the Palermo "Falcone-Borsellino" International airport. The "La Torre" complex is situated after the large semi-circular beach of Mondello, just a few metres on the other side of the fishing village, on a little promontory of which the hotel occupies the smaller part, overlooking the bay with its park stretching out in the opposite direction as far as the "Capo

Splendid Hotel "La Torre"

Swimming pool inside "La Torre"



Gallo" coastal reserve. Over there you will find all aquatic sports (sailing, windsurfing, water-biking, motor-boating, diving, etc).
Further details on the Hotel can be found at www.latorre.com.

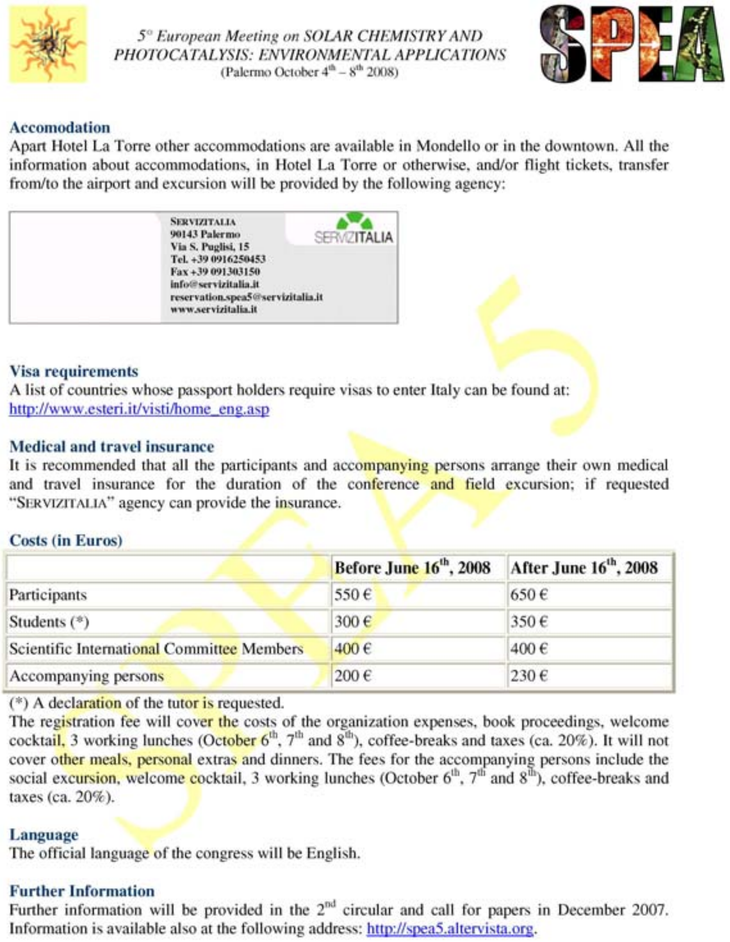
Important dates
Friday May 2nd 2008: Deadline for submission of abstracts;
Monday June 2nd 2008: Acceptance of the abstracts and communication to the authors of the modality of presentation (Poster or Oral);
Monday June 16th 2008: Deadline for reduced conference fees payment;
Monday June 30th 2008: Deadline for hotel reservations;
Saturday October 4th 2008: Arrival, accommodation and registration;
Sunday October 5th 2008: Registration, social excursion, welcome cocktail;
Monday October 6th 2008: Plenary lectures, oral communications and poster sessions; meeting of the Scientific International Commettee;
Tuesday October 7th 2008: Plenary lectures, oral communications and poster sessions; social dinner;
Wednesday October 8th 2008: Plenary lectures, oral communications, closing session and deadline for submission of full papers.

Conference facilities
The conference hall will be equipped with PC connected to a multimedia projector and overhead projector for powerpoint presentation or slide projection. Authors are recommended to prepare their oral presentation on CD or on USB pendrive. Posters should be exhibited on standard 100x120 cm (LxH) sheets.
Refreshments will be provided in a room behind the Conference Hall. Posters will be displayed in a hall near the Conference Hall, making possible their viewing and discussion throughout the conference. The registration desk will be open for information and assistance throughout the conference.

Accompanying persons:
Visits to the most important landmarks near Palermo (e.g., Segesta, Erice, Agrigento etc) will be scheduled (the excursion will be carried out only if a minimum number of participants is reached). The relative costs will be published on the website prior to the conference.

Transport
Palermo "Falcone-Borsellino" airport is well-served with regular flights from the main Italian cities (Milan, Turin, Rome, Bologna) and from many European cities (e.g. Madrid, London, Paris, Budapest). The connection between the airport and Hotel La Torre Mondello (about 20 km) will be by bus, by metro/bus or by taxi (ca. 50 euros).
Bus transfers to the Hotel "La Torre" from and to the airport will be scheduled on Saturday October 4th 2008 (about at 8.00 PM) and on Wednesday October 8th 2008 (after the closing session). All the information will be available on the conference website http://spea5.altervista.org/.

Weather
Weather in Sicily is usually pleasant, sunny and calm during October, but sometimes little rain occurs. Temperature ranges between 15-25°C.



5° European Meeting on SOLAR CHEMISTRY AND PHOTOCATALYSIS: ENVIRONMENTAL APPLICATIONS
(Palermo October 4th – 8th 2008)

Accomodation

Apart Hotel La Torre other accommodations are available in Mondello or in the downtown. All the information about accommodations, in Hotel La Torre or otherwise, and/or flight tickets, transfer from/to the airport and excursion will be provided by the following agency:

SERVIZITALIA
90143 Palermo
Via S. Puglisi, 15
Tel. +39 0916250453
Fax +39 091303150
info@servizitalia.it
reservation.spea5@servizitalia.it
www.servizitalia.it

Visa requirements

A list of countries whose passport holders require visas to enter Italy can be found at:
http://www.esteri.it/visti/home_eng.asp

Medical and travel insurance

It is recommended that all the participants and accompanying persons arrange their own medical and travel insurance for the duration of the conference and field excursion; if requested "SERVIZITALIA" agency can provide the insurance.

Costs (in Euros)

	Before June 16th, 2008	After June 16th, 2008
Participants	550 €	650 €
Students (*)	300 €	350 €
Scientific International Committee Members	400 €	400 €
Accompanying persons	200 €	230 €

(*) A declaration of the tutor is requested.

The registration fee will cover the costs of the organization expenses, book proceedings, welcome cocktail, 3 working lunches (October 6th, 7th and 8th), coffee-breaks and taxes (ca. 20%). It will not cover other meals, personal extras and dinners. The fees for the accompanying persons include the social excursion, welcome cocktail, 3 working lunches (October 6th, 7th and 8th), coffee-breaks and taxes (ca. 20%).

Language

The official language of the congress will be English.

Further Information

Further information will be provided in the 2nd circular and call for papers in December 2007. Information is available also at the following address: http://spea5.altervista.org.

Lecture Conference of the GDCh-Fachgruppe Photochemie
October 6th to 8th, 2008, Bielefeld, Germany

INFORMATION

REGISTRATION

Registration will start with the second circular (approx. June 2008). To obtain the second circular, please register at the online-news-list at:

http://fachgruppe-photochemie.de

INFORMATION ABOUT THE SCIENTIFIC PROGRAMME AND THE ORGANISATION

Prof. Dr. Jochen Mattay
Universität Bielefeld
Institut für Organische Chemie I
Universitätsstr. 25
D-33615 Bielefeld

Phone: +49 521 106-2072
Fax: +49 521 106-6417
E-Mail: mattay@uni-bielefeld.de

INFORMATION ABOUT ABSTRACT SUBMISSION AND REGISTRATION

Gesellschaft Deutscher Chemiker e.V.
(German Chemical Society)
Congress Team / Photochemie 2008
P.O. Box 90 04 40
D-60444 Frankfurt am Main

Varrentrappstr. 40-42
D-60486 Frankfurt am Main

Phone: +49 69 7917-366 (Claudia Birkner)
Fax: +49 69 7917-475
E-Mail: tg@gdch.de
Internet: www.gdch.de

Executive Director: Prof Dr. Wolfram Koch
Registernummer beim Vereinsregister: VR 4453 Registergericht Frankfurt am Main

INVITATION

GDCh
GESELLSCHAFT DEUTSCHER CHEMIKER

Fachgruppe Photochemie

21. Lecture Conference

in cooperation with
Deutsche Bunsengesellschaft
für Physikalische Chemie

October 6 – 8, 2008 · Bielefeld

Fachgruppe Photochemie

Deutsche Bunsengesellschaft für Physikalische Chemie

INVITATION

The division Photochemistry of Gesellschaft Deutscher Chemiker e. V. (German Chemical Society) in cooperation with Deutsche Bunsengesellschaft cordially invites you to participate in the

21. Lecture Conference
with special symposium
"Photochemistry in the Material Sciences"

VENUE

University of Bielefeld
Universitätstr. 25
D-33615 Bielefeld

SCIENTIFIC COMMITTEE

M. Goez	University of Halle/D
A. G. Griesbeck	University of Cologne/D
G. Knör	University of Linz/A
K. Kohse-Höinghaus	University of Bielefeld/D
J. Mattay	University of Bielefeld/D
K. Meerholz	University of Cologne/D (Chairman of the Division)
W. Nau	Jacobs University of Bremen/D
G. Wagenblast	BASF AG, Ludwigshafen/D

LOCAL COMMITTEE

J. Mattay	University of Bielefeld

THEODOR-FÖRSTER-MEMORIAL-LECTURE/ ALBERT-WELLER-PRIZE

The Theodor-Förster-Memorial-Lecture and the award of the Albert-Weller-Prize will take place on October 7, 2008.

INVITATION

KEYNOTE LECTURES

Kevin Booker-Milburn	University of Bristol/UK
Dirk Guldi	University of Erlangen-Nürnberg/D
Masahiro Irie	Rikkyo University of Tokyo/J
Stephan Landgraf	Technical University of Graz/A
Klaus Müllen	MPI for Polymerresearch, Mainz/D
Markus Sauer	University of Bielefeld/D
Pablo Wessig	Humboldt University of Berlin/D
Hartmut Yersin	University of Regensburg/D

ORAL COMMUNICATIONS AND POSTERS

Please submit your scientific contribution exclusively via internet at

http://fachgruppe-photochemie.de

A sample abstract is to be found on this website. No revisions or corrections will be made by the scientific committee.

After a successful transmission you will receive a reference code for each submitted paper and a few days later a confirmation of receipt. In case you should not have received this confirmation after two weeks please contact GDCh by e-mail tgonline@gdch.de and indicate the reference code of your paper.

The scientific committee reserves the right to accept or reject papers, and to assign them to oral or poster contribution.

DEADLINES

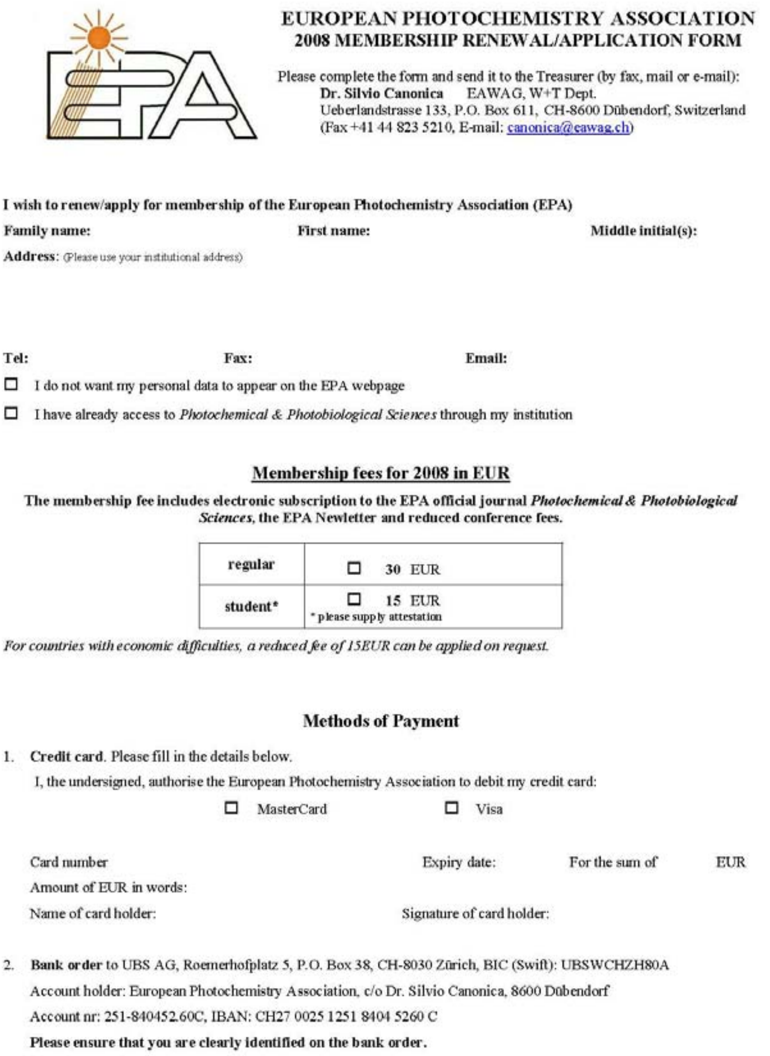
Submission of oral contributions: May 21, 2008
Submission of posters: August, 6, 2008

SCHOLARSHIPS

It is planned to offer scholarships to a limited number of students, candidates for doctor's, diploma's, bachelor's or master's degree presenting a scientific contribution (main author of an oral contribution or poster). Please send your application to GDCh until **August 6, 2008**, latest. The form is to be found at

www.gdch.de/stipendien

MEMBERSHIP APPLICATION FORM



EUROPEAN PHOTOCHEMISTRY ASSOCIATION
2008 MEMBERSHIP RENEWAL/APPLICATION FORM

Please complete the form and send it to the Treasurer (by fax, mail or e-mail):
Dr. Silvio Canonica EAWAG, W+T Dept.
Ueberlandstrasse 133, P.O. Box 611, CH-8600 Dübendorf, Switzerland
(Fax +41 44 823 5210, E-mail: canonica@eawag.ch)

I wish to renew/apply for membership of the European Photochemistry Association (EPA)

Family name: **First name:** **Middle initial(s):**

Address: (Please use your institutional address)

Tel: **Fax:** **Email:**

☐ I do not want my personal data to appear on the EPA webpage

☐ I have already access to *Photochemical & Photobiological Sciences* through my institution

Membership fees for 2008 in EUR

The membership fee includes electronic subscription to the EPA official journal *Photochemical & Photobiological Sciences*, the EPA Newletter and reduced conference fees.

regular	☐ **30** EUR
student*	☐ **15** EUR * please supply attestation

For countries with economic difficulties, a reduced fee of 15EUR can be applied on request.

Methods of Payment

1. **Credit card**. Please fill in the details below.
   I, the undersigned, authorise the European Photochemistry Association to debit my credit card:
   ☐ MasterCard ☐ Visa

   Card number Expiry date: For the sum of EUR
   Amount of EUR in words:
   Name of card holder: Signature of card holder:

2. **Bank order** to UBS AG, Roemerhofplatz 5, P.O. Box 38, CH-8030 Zürich, BIC (Swift): UBSWCHZH80A
   Account holder: European Photochemistry Association, c/o Dr. Silvio Canonica, 8600 Dübendorf
   Account nr: 251-840452.60C, IBAN: CH27 0025 1251 8404 5260 C
   Please ensure that you are clearly identified on the bank order.