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Photochemistry Association

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EDITORIAL

President's Letter

The EPA Newsletter continues with the tradition of reporting activities in the field of photochemistry from different European countries. You will find in the present printed issue, which appears alternately with an electronic issue, news from Spain (page 32) and Denmark (page 56). This time, even non European countries have contributed with abstracts of PhD theses. The abstracts of the young Doctors nominated for the second Prize for the best PhD thesis in the field of Photochemistry are gathered together (page 69). Particular emphasis is given to the work of the winner, Anne Kotiaho from the Tampere University of Technology (page 18).

Anne Kotiaho will receive her Prize and will give a talk at the XIIIrd IUPAC Symposium on Photochemistry at Ferrara. Furthermore, at this Symposium, Werner Nau, winner of the EPA/Photochemical & Photobiological Sciences award will present his work. Another important lecture will be given by David Phillips who is the recipient of the Porter Medal.

At Ferrara, we will also hold our General Assembly on July 12th. There, I will present a report of the last three years' activities of the present Executive Committee and then, a new President and a new Committee will be elected. According to the statutes approved two years ago (page 10), the future President must have served in the Executive Committee so as to be familiar with the matters to be handled. Eric Vauthey from the University of Geneva has accepted the nomination as candidate (page 8). The General Assembly will be followed by an EPA reception offered to all members.

This will be my last letter as EPA President. Holding such a position has been an honour for me, making a collective effort with my colleagues of the Executive Committee a great pleasure. As Past President, I would like to focus my activity in the Executive Committee during the next two years in order to make photochemistry known to the wide public. This project (page 16), started in 2008, will be outlined in my talk "Tweets of the European Photochemistry" which will be presented in the satellite conference dedicated to Giacomo Giamician and Emanuele Paternò.

Dr Dimitra Markovitsi
CNRS Research Director

PRESIDENTIAL CANDIDATE'S LETTER

If I am elected as EPA President, my main objective for the two coming years, will be essentially to consolidate the changes and to reinforce the new activities that have been initiated by the past and the present Presidents, David Phillips and Dimitra Markovitsi, and the executive committee (EC). One has to admit that over the past years, EPA had slowly fallen into lethargy. One of the reasons for this is that photochemistry has made a transition from being a new area of sciences into having become a mature field. Therefore, photochemistry has expanded in many different directions, such as single molecule spectroscopy, photomedicine, or photonics, to cite a few, and because of this, the number of scientists viewing themselves as photochemists has been continuously decreasing.

I consider as a priority for the coming years to convince those working with light and molecules that EPA is the community where they will meet the people and will have access to the knowledge they need for progressing in their research. The main tools for this are:

- the Newsletter, to share and exchange practical know-how, to advertise the activities of our members, to encourage young researchers to present their work;
- the webpage to share information between members but also to expose our activities to non EPA members;
- the photochemistry conferences: to be an EPA member gives some direct 'privileges' such as reduced conference fees. Events such as the one that will be organised during the next IUPAC photochemistry conference in Ferrara are a particularly pleasant way to meet new colleagues and to exchange ideas.
- our journal PPS: despite the present frenzy on impact factor and other esoteric bibliometric parameters, we should not forget that, in order to make a journal attractive and visible, we have ourselves to publish our best research there.

Such an objective requires substantial effort and, of course, I won't be able to reach it alone. Indeed, the EC is playing a crucial role in making these ideas possible. The new EC will comprise some present and experienced members that are willing to serve further and new members that will most certainly bring fresh ideas.

I hope that we will be able to continue the remarkable work accomplished by Dimitra Markovitsi and the present EC and that to be an EPA member will become more and more an evidence for a photo-molecular scientist.

Prof. Eric Vauthey
Department of Physical Chemistry
University of Geneva

THE STATUTES OF THE EUROPEAN PHOTOCHEMISTRY ASSOCIATION

TITLE I: Name, Headquarters, Permanence and Objects

ARTICLE 1

- (a) An incorporated organisation under the name of the European Photochemistry Association (EPA) has been set up under the provisions of the Swiss law.
- (b) It is a permanent body.
- (c) Its headquarters are in Zürich.
- (d) In the event that EPA is disbanded, the remaining finances must ultimately be transferred to an organisation having the same or similar aims. A distribution of the funds among its members is excluded.

ARTICLE 2

- (a) The EPA is established to promote and encourage the international development of photochemistry and related subjects with special reference to European and neighbouring countries. The Association is concerned with all experimental and theoretical aspects of the interaction of light with molecular systems. These range from basic knowledge and practical know-how to applications in areas such as materials science, biology, medicine and the environment.
- (b) In particular, the aims to be pursued by EPA are:
 - (1) Promotion of co-operation between European photochemists in universities, research centres and industry through fostering international contacts and European exchange.
 - (2) Encouragement, stimulation and co-ordination of meetings in Europe.

- (3) Educational activities including summer schools, workshops and incorporation of photochemistry into the curricula of universities.
- (4) Promotion of photochemical literature.
- (5) Promotion of photochemistry with funding agencies.
- (6) Promotion of awareness of photochemistry and its applications to the wider public.

TITLE II: Membership

ARTICLE 3

- (a) Membership of EPA is open to all scientists both from Europe and from countries outside Europe.
- (b) Membership is annual and is subject to a fee as assessed by the Executive Committee and approved by the General Council. Membership fees must be paid according to the rules established by the Executive Committee.
- (c) It is the responsibility of the members to provide and maintain correct contact details, including email addresses. Changes should be notified to the General Treasurer.
- (d) EPA members of a given country may organize, by agreement with the Executive Committee, a national EPA section with a designated national representative who serves as a contact person.
- (e) A national section may lose its status upon the decision of the Executive Committee.

ARTICLE 4

Membership implies compliance with the decisions and resolutions made by the General Council and the Executive Committee as provided in the statutes

ARTICLE 5

Membership of EPA may be terminated at the request of the

Executive Committee for just reason.

ARTICLE 6

Members are not personally liable for the contracted debts of the EPA; liability is limited to the assets of the association.

ARTICLE 7

The organs of the EPA are the General Council and the Executive Committee.

ARTICLE 8

(a) The General Council consists of all members of the EPA and is its supreme organ.

(b) The General Council has the following rights and functions:

- (1) To agree and to alter the statutes.
- (2) To decide about the amounts of the annual contributions (membership fees), following the proposal of the Executive Committee.
- (3) To vote on the annual reports of EPA activities and finances presented to it by the Executive Committee.
- (4) To elect biennially from among its ordinary members the Executive Committee.
- (5) To elect biennially two auditors who must prepare a report on the financial situation of EPA and ensure proper management of financial affairs by the Executive Committee.

(c) The General Council should meet at least biennially, usually in connection with an international scientific meeting, to discuss the agenda, which may be proposed by all members, to determine the general policy of EPA and to exercise its rights according to ARTICLE 8b. This meeting should be organised by the Executive Committee.

(d) At the request of 20% of all EPA members, an extraordinary meeting of the General Council must be organised, and at least three month's notice given, by the Executive Committee. Due provision must be made for those who can not attend the extraordinary meeting of the General Council personally to express their opinion in writing and, if necessary, by postal or electronic vote.

(e) A resolution for winding-up or merger of EPA must be put to a meeting of the General Council, which if it agrees will instruct the Executive Committee to ballot all members of EPA. Such a resolution can only be passed by a majority of not less than two-thirds of the votes cast. In winding-up the General Council should decide whether to dispose of the balance of the assets of EPA to a similar scientific body.

ARTICLE 9

(a) The Executive Committee administers EPA.

(b) The Executive Committee consists of the President, the past-President, the Vice President, the General Treasurer and up to six other members who may be responsible of a specific function at the discretion of the President. Exceptionally, additional members can be co-opted by the Executive Committee to fulfil specific roles.

(c) The tasks of the Executive Committee include in particular:

- (1) The achievement of the aims of EPA as outlined in ARTICLE 2.
- (2) The management of the property of EPA including gifts and legacies left to EPA.
- (3) The preparation of an annual report on the activities of EPA and on the financial accounts which must be presented to the General Council together with an auditor's report.
- (4) The convening of the General Council and/or the individual consultation of the members in accordance with these statutes.
- (5) The execution of the decisions of the General Council.
- (6) The organisation of the biennial elections for the Executive Committee (as outlined in ARTICLE 9f).

(d) Formal decisions of the EPA require the signature of the President or, exceptionally, of the Vice-President in order to be binding. The President shall have power to delegate certain of his/her powers to other members of the Executive Committee.

(e) The term of office for an elected member of the Executive Committee is normally two years. Re-election is permitted up to a maximum of three consecutive terms.

(f) The Executive Committee organizes elections for its own succession

- (1) Elections take place normally by a show of hands at the General Council (or exceptionally, by electronic voting).
- (2) The candidate(s) for President must normally be a member of the Executive Committee in office.
- (3) The candidate(s) for President will present a program for the EPA's future activities and actions and for the efficient functioning of the Executive Committee.
- (4) Not less than one month prior to the election, the Executive Committee will publicise to EPA members the name(s) of the candidate(s) for President and their program(s).
- (5) Members may nominate themselves or other EPA members with their consent for election to the Executive Committee. Nominations should be made in writing, signed by the nominee, to the Executive Committee any time up to one month prior to the General Council.

TITLE IV: Finances

ARTICLE 10

(a) EPA is a non-profit making organisation.

(b) The income of the EPA shall consist of:

- (1) Contributions of members as assessed by the General Council.

- (2) Contributions from governmental bodies or national scientific societies representing member countries.
- (3) Gifts, donations, and legacies.
- (4) Grants, which may be accorded to it.
- (5) Royalties from publications.
- (6) Revenues from advertisements in publications.

ARTICLE 11

(a) A national section may hold an account to which EPA members pay their dues and where other official revenues and expenses are recorded.

(b) The person in a national EPA section responsible for the finances may be the national Local Treasurer. Local Treasurers are appointed by the Executive Committee.

(c) The Local Treasurer of a national EPA section sends a yearly report and justifications to the EPA General Treasurer. They transfer official revenues to the account of EPA International according to the requirements of the Executive Committee.

TWEETS OF EUROPEAN PHOTOCHEMISTRY

Making photochemistry known to the wider public is vital for our discipline. There is no doubt that today many colleagues who would have considered themselves as photochemists in the past are members of groups dealing with applications as defined by national and European scientific policies (environmental chemistry, nanotechnologies, health technology...) rather than those dealing with the processes being studied. Although applications are obviously important, we should not forget that there is a common basis in the work involving interaction of light with molecular systems. Bringing these aspects together would reinforce the necessity of a shared scientific culture and attract students towards our luminous discipline. In addition, highlighting the various facets of photochemistry, and in particular the connexion between primary processes and applications, would bring recognition by research and funding bodies.



The opportunity for EPA to get involved in an activity aiming at the popularisation of photochemistry was provided by the e-knownet project supported by the European Lifelong Learning Programme (2008-2010). The aim of e-knownet, whose full title is «Network for ICT-enabled non-formal science learning» (ICT: Information and Communication Technologies), is to develop an innovative and viable mechanism able to facilitate the flow of new scientific knowledge produced in the research laboratory, to larger, non-expert segments of society, in forms suitable for non-formal learning.

The project is coordinated by *Eugenides Foundation*, a science centre and a landmark of science and technology popularisation based in Athens, Greece. The other partners are: the *Greek Research and Technology Network* (Athens, Greece), the *Center for Digital Systems, Competence Center e-Learning/Multimedia, Frei Universität* (Berlin, Germany) the *Science Communication Observatory / Universitat Pompeu Fabra* (Barcelona, Spain) and the *Francis Perrin Laboratory*. The first four partners have expertise in science learning and ICT, while the

Francis Perrin Laboratory (<http://www-lfp.cea.fr/>) conducts research in the field of physical chemistry, most of the research topics involving interactions of light with molecular systems.

The visible outcome of the project will be a web-based platform called “sciencetweets”. This tool will be completed by the end of 2010 but some “digital exhibits” will be on line by July. Behind the portal, there is an important methodological work with the objective to find the optimum way to transform rapidly recently published research results to e-material (combining text, images, videos, web resources...) understandable by different target groups (adults, school students, science educators).

In the initial proposal, the “digital exhibits” were supposed to come exclusively from the Francis Perrin Laboratory. By the time the proposal was accepted, I became President of the European Photochemistry Association and suggested to involve in the project this Association which became an official stakeholder. David Phillips was appointed to the scientific board of the project and members of the EPA Executive Committee (David Phillips, Sandra Monti and Werner Nau) contributed research examples from their own laboratories. A particular effort is being made currently to explain in simple words and images some basic principles of photochemistry.

By the end of the project, the European Photochemistry Association will judge the compatibility of the pilot platform with its aims and will decide whether “sciencetweets/photochemistry” can function



entirely under its responsibility. This would allow all EPA members to show their work on the portal, gathering together different aspects of photochemistry.

Dimitra Markovitsi
Head of the Francis Perrin Laboratory, CEA-CNRS URA 2453,
CEA/Saclay, France
President of the European Photochemistry Association

EPA PHD PRIZE

EPA prize for PhD Thesis on Photochemistry

The second EPA Prize will be attributed during the XXIIIrd IUPAC Symposium on Photochemistry which will be held in Ferrara, Italy in 2010. This year the winner of the PhD Prize is Anne Kotiaho from Tampere.

Anne Kotiaho

Gold Nanoparticle-Chromophore Systems: Assembly and Photophysical Interactions

Tampere University of Technology, Finland
Supervisor: Prof. Helge Lemmetyinen

Gold nanoparticle-chromophore systems were prepared using two assembly strategies: thin films and functionalization of the metal cores with chromophores. These assemblies were studied with steady-state and time-resolved spectroscopic techniques and the thin films also with photoelectrical and microscopic methods.

Controlled assembly of gold nanoparticles and chromophores into solid structures is necessary for building photoactive devices but the design of applications relies on knowledge of photoinduced processes within the gold nanoparticle-chromophore systems. Alternating thin films of gold nanoparticles and chromophores were prepared using Langmuir-Blodgett and – Schäfer techniques. The photoelectrical measurements indicate that the particles can function either as electron acceptors or donors to the photoexcited chromophores, demonstrating the active role of the gold cores in photoinduced charge transfer reactions in films. Photoinduced electron transfer takes place from a poly(hexylthiophene) layer to an adjacent gold nanoparticle layer, and in the case of a porphyrin or a fullerene layer, the gold nanoparticles donate electrons to these chromophores. While photoelectrical measurements demonstrated charge transfer in the films of porphyrins and gold nanoparticles, also

energy transfer was considered to be possible. Time-resolved spectroscopic measurements showed that most, more than 80%, of the photoexcited porphyrins decay by energy transfer to the gold nanoparticles, whereas charge transfer is a minor relaxation route. Both energy and charge transfer processes are known to take place in chromophore-gold nanoparticle systems and in the case of porphyrin-gold nanoparticle films the relative importances of these two processes could be estimated.

The highest photoelectrical signal was observed for films combining gold nanoparticles and porphyrin-fullerene dyads. Films of porphyrin-fullerene dyads and gold nanoparticles are a step towards the construction of both structurally and functionally more complex systems. Porphyrin-fullerene dyads are known to undergo intramolecular photoinduced charge transfer via an exciplex intermediate state. Certain type of porphyrin-fullerene dyads can organize in Langmuir films, and thus the porphyrin moieties of the dyad are located on their own plane adjacent to the plane formed by the fullerene moieties. A gold nanoparticle layer enhances charge transfer of the dyad significantly, when placed near the porphyrin moieties of the dyads. In addition, fluorescence measurements indicated that the adjacent gold nanoparticle layer affects the relaxation of the exciplex state of the dyad.

The thin film strategy followed was successful in organizing the particles and chromophores at close distances. The way to control even better their organization is to attach the chromophores directly to the metal core surface. Porphyrin- and phthalocyanine-functionalized gold nanoparticles were prepared using a ligand exchange method. Photoexcited porphyrins transfer energy very rapidly, in few picoseconds, to the gold cores as shown by time-resolved fluorescence measurements. The packing of the porphyrins on the gold nanoparticle surface and their fluorescence lifetimes are dependent on position of the linkers on the porphyrin molecule.

The phthalocyanine-functionalized gold nanoparticles offered a possibility to study the photoinduced processes in more detail because both of the components could be excited nearly selectively. Time-resolved absorption measurements were used to study their fast photoinduced processes. Selective excitation of the phthalocyanines leads also to electron transfer to the gold cores, and most likely also to energy transfer. The role of gold cores as energy acceptors in chromophore-functionalized gold nanoparticles has been widely

studied and reported, whereas observations of gold cores acting as electron acceptors are few. Selective excitation of the gold cores in phthalocyanine-functionalized particles results in energy transfer to the phthalocyanines, demonstrating that the gold cores can behave as energy donors.

These results show that although the photoinduced processes of gold nanoparticle-chromophore systems are generally known, they are strongly affected by the choice of the chromophore and by the design of the system. The next step in assembling chromophores and gold nanoparticles would be to organize functionalized gold nanoparticles into solid structures. These systems offer many possibilities for controlling organization and thus the rates of photoinduced processes. Tunable parameters could include, for example, size and choice of the metal nanoparticle, choice of the chromophores, orientation and distance of the chromophore relative to the metal core and excitation energy. The gold nanoparticle-chromophore systems are a fragment of the booming area of nanotechnology that is and continues to develop, more and more as a part of everyday life and not just something from the pages of science fiction books.

GRAMMATICAKIS-NEUMANN PRIZE 2010

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 2011.

The Prize consists of a diploma and a financial award of 5'000 Swiss Francs (for each awardee, if there is more 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, molecular photobiology, or molecular photophysics.

The Prize, for which nominations are now being invited, will be presented during the 2010 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 official EPA journal, *Photochemical and Photobiological Sciences*.

Each member of the EPA, or one of its sister organizations (such as the Inter-American Photochemical Society) can nominate an individual as candidate for the Grammaticakis-Neumann Prize. Such nominations, accompanied by supporting documentation (detailed justification, curriculum vitae, list of publications, and at least two supporting letters), should be submitted by e-mail (with attachments) to the executive director of the Swiss Chemical Society, Dr. Lukas Weber (weber@scg.ch). The closing date for nominations is October 10, 2010 (see also www.scg.ch/awards/grammaticakis.html).

Previous laureates of the Grammaticakis-Neumann Prize are Sivaguru Jayarman (2009) Alexander Heckel (2008), Alberto Credi (2007), Torsten Fiebig and Achim Wagenknecht (2006), Dario Bassani (2005), Johan Hofkens (2003), 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). In other years (e.g. 2002 and 2004) no prize was awarded, because no suitable candidate was proposed.

PERSONAL NEWS

The Porter Medal 2010, Professor David Phillips OBE

It is a pleasure to announce that Professor David Phillips has been awarded the Porter Medal this year, the first British scientist to do so since its inauguration in 1988. David is well known within the photochemistry community, having led a long and distinguished career in the field. He has made significant contributions across a broad range of areas ranging from high-resolution spectroscopy through to photobiology. He has published over 300 research papers as well as numerous reviews, book chapters and textbooks, a total of more than 570 publications.

David's scientific career began when he moved from his home town of South Shields in the North East to study chemistry at the University of Birmingham. He stayed on at Birmingham for his PhD, examining the reactions of photolytically generated free-radicals. Following this he was awarded a Fulbright Fellowship where he worked as a post-doc with Albert Noyes (1964-66) at the University of Texas at Austin, moving to the Institute of Chemical Physics in Moscow funded by a Royal Society /Academy of Science USSR Exchange Fellowship (1966-67). Returning to the UK he was appointed as a lecturer at University of Southampton where he stayed from 1967 – 1979.

David was appointed as the Wolfson Professor and Deputy Director of the Royal Institution of Great Britain in 1979, working with the Director Lord Porter FRS, Nobel Laureate. The presence of the two professors and their complementary research interests at the Royal Institution made it a centre of excellence for photochemistry, and the destination of the many distinguished international visitors. Interestingly despite their common interests in photochemistry and the fact that they used similar techniques Phillips and Porter only share two publications! It was during his time at the Royal institution that David was able to develop his interest in the public

understanding of science, giving demonstration lectures to young and old alike. His demonstration lectures were highly acclaimed and he travelled all over the world with his packing case of demonstration equipment – anyone who has seen him lecture will recall his celebrated ‘glass-baby’ that he used to demonstrate the use of UV-phototherapy for neonatal jaundice and the fact that addition of gin, ice and lemon does not result in the quenching of fluorescence from tonic water. In 1986 he jointly presented the Royal Institution Christmas lectures with Sir John Thomas on the subject of “Crystals and Lasers”.

Following Porter’s retirement from the RI and the appointment of Sir John Thomas as the director in 1986 the research focus of the institution changed. With some reluctance David decided to move from the RI, taking up the chair of Physical Chemistry at Imperial College in

1989 and then becoming the Head of Department in 1992. Under his leadership chemistry at Imperial College went from strength to strength, securing its position as one of the top chemistry departments in the UK and indeed the world. After an incredible 10 years as the Head of Department David became the Hoffman Professor of Chemistry and Dean of the Faculties of Life Sciences and Physical Sciences at Imperial College. In his retirement he continues to work at Imperial College as an Emeritus Professor of Chemistry and Senior Science Ambassador to Schools at Imperial College, two posts that reflect his ongoing commitment and interest in research and scientific education respectively.

David’s long and distinguished career in chemistry have been rewarded on numerous occasions, including the RSC Nyholm Medal (1994), the BD Shaw medal (2005), the Michael Faraday award of the Royal Society of London for public understanding of science (1999) and an OBE birthday honours for his services to science education (1999). Fittingly, as an ambassador for the subject of chemistry and the public understanding of the subject David has been elected to the post of president of the Royal Society of Chemistry which he takes up in 2010.

The award of the Porter metal acknowledges major contributions David has made throughout his career and is a symbol of recognition from peers and colleagues across the world.

David's early work was in the field of gas phase spectroscopy and photochemistry, a topic for which he never lost interest. He was one of the first to adopt the technique of supersonic jet spectroscopy, a technique in which molecules are squirted to a small nozzle into a vacuum chamber. In the expanding jet of gas molecules cooled to extremely low rotational and vibrational temperatures making the absorption spectra of poly-atomic molecules highly simplified unstructured. Using high-resolution laser induced fluorescence it is possible to obtain detailed structural information. As one is looking at isolated molecules it is possible to sequentially introduce solvent species to produce van der Waals and hydrogen bonded species in order to understand the process of solvation. David's group used supersonic jet spectroscopy to investigate the photophysical processes of molecules that exhibit intramolecular charge transfer, ICT, states with a view to understanding enigmatic dual fluorescence of compounds such as 4-amino-benzonitrile.

One of the key measurements in fluorescence spectroscopy is the determination of fluorescence lifetime. The technique of time correlated single photon counting, TCSPC, had been established as a means of determining this value, however, until the 1970s it employed low intensity hydrogen or nitrogen flash lamps as the excitation source.

These were notoriously difficult to work with and had frustratingly low light output and repetition rates. Recognizing the possibility of lasers as light sources David from the first groups in the world to employ cavity dumped and mode locked lasers at excitation sources. The impact of these high-intensity high-frequency sources upon the field cannot be underestimated – measurement is now considered to be routine. With his colleague Desmond O'Connor he wrote the monograph "Time Correlated Singlet Photon Counting" which remains the definitive work in the field some 26 years later! This book continues to be highly cited.

As well as pioneering the use of lasers for the technique he employed it for the study of a wide variety of fluorescent systems, including the study of polymer and protein dynamics, charge transfer systems and fundamental photophysical behaviour, as well as the determination of fluorescence lifetime in cellulose. His most recent work includes the development of one and two-photon fluorescence lifetime imaging, demonstrating a long and sustained contribution to this vital technique.

In the early 1980s David began studies of phthalocyanine derivatives that had been proposed as photo bleaching agents to be incorporated into domestic washing products. Realizing the potential of these compounds to sensitise singlet molecular oxygen, which in turn is cytotoxic David suggested that they may be potent photosensitiser for photodynamic therapy, PDT, which at the time was emerging as a potential treatment for certain types of cancer. David established collaborations with biologists and medics, embarking upon a long-term investigation into the potential role of phthalocyanines as PDT agents. Over the past 30 years his publications in this area demonstrate the progression from detailed investigations of photophysical behavior, their phototoxicity through to their efficacy in vitro and in vivo. Characteristically his contribution to the field is significant and diverse, after realizing the potential for photodynamic agents to act as a photo-inhibitor of viral bacterial and fungal agents he patented the "laser-toothbrush", and more recently led to the formation of a spin out company, Photobiotics with the aim of bringing photodynamic products to the marketplace.

David is a champion of in the development of UK national facilities, particularly the development of the Central Laser Facility based at the Rutherford Appleton Laboratory. In the mid 1980s he worked with staff at RAL to develop nanosecond time-resolved resonance Raman spectroscopy, which he used to investigate the fundamentals of electron transfer reactions. Pushing technology to the limit he pushed towards the picosecond time domain, leading to great advances in our understanding of early relaxation dynamics of excited states. He also uses techniques to complement his gas phase measurements of intramolecular charge transfer processes, finding some evidence to support the controversial twisted intramolecular charge transfer or TICT state. In later years David was also a strong advocate for the

development of complementary ultrafast time resolved infrared absorption and transient absorption instrumentation at the laboratory

David is one of the gentlemen of science. As a supervisor he always provided young researchers with an environment in which they could flourish giving individuals the opportunity to try their own ideas.

During the course of his academic career he has supervised more than 50 PhD students and 40 post-doctoral fellows, as well as hosting countless visitors to the group. A significant fraction of the Phillips family have gone on to academic posts, and by now David must be an academic 'great-grandfather'! It is no accident that at every photochemistry conference or meeting there is a group of Phillips group members who meet-up and socialize and recollect tales of their time spent in the group.

David continues to perform research and in 2009 contributed to 3 articles stemming from his continued interest in fluorescence imaging to study cellular chemistry. He continues his passion for championing the national and international public awareness of science through his highly regarded public lecture programmes. Working hard in encouraging school children and his series entitled "Light Relief" and "Braving The Elements", with the former putting photochemistry squarely in the mind of budding 12 year old scientists. When presenting these lectures David is in his element able to enthral the audience with his passion of chemistry through the eyes of a photochemist. His demonstration lectures both entertain and educate with their wide popularity is shown by David making a staggering 19 presentations in 2009!

A favourite tale to recall is from his time at Imperial College when David was frustrated by the late arrival of a vacuum-line from the glass-workshop for one of his final year project students. He asked that we get hold of some glass tubing, taps and a gas-torch so he could make one himself.

Doing so, an audience of post-docs and students gathered to watch in awe as David assembled a rudimentary but perfectly functional vac-line. He explained that as a post-doc he'd had to do this many

times himself and, just like riding a bicycle he'd never lost the knack – students take note, you never know what your supervisor can do!

Selected Publications.

- 1) SR Meech and D. Phillips, "Photophysics Of Some Common Fluorescence Standards", *J. Photochem.* (1983) 23 193-217
- 2) "Time-Correlated Single Photon Counting" by D.V. O'Connor & D. Phillips, Academic Press, London, (1984).
- 3) K. P. Ghiggino, A. J. Roberts, D. Phillips, "Time-resolved Fluorescence Spectroscopy Using Pulsed Lasers", *J. Phys. E-Scientific Instruments*, (1980) 13, 446-450.
- 4) S. Dhimi, A.J. DeMello, G. Rumbles, S.M. Bishop, D. Phillips and A. Beeby, "Phthalocyanine Fluorescence at High Concentration – Dimers or Reabsorption Effect", *Photochem. Photobiol.* (1995) 61 341-46
- 5) W. J. Feast, I. S. Millichamp, R. H. Friend, M. E. Horton, D. Phillips, S. D. D. V. Rughooputh, G. Rumbles. "Optical-Absorption and Luminescence in Poly(4,4'-Diphenylenediphenylvinylene)", *Synth. Metals* (1985) 10, 181-191.
- 5) K. Suhling, P. M. W. French and D. Phillips, "Time-resolved fluorescence microscopy", *Photochem. Photobiol. Sci.*, (2005) 4, 13-22.
- 6) J. N. Moore, D. Phillips and R. E. Hester, "Time-resolved Resonance Raman-Spectroscopy Applied to the Photochemistry of the Sulfonated Derivatives Of 9,10-anthraquinone", *J. Phys. Chem.* (1988) 92, 5619-5627.
- 7) E. Vauthey, A.W. Parker, B. Nohova, D. Phillips, "Time-resolved Resonance Raman-Study of the Rate of Separation of a Geminate Ion-Pair Into Free Ions in a Medium Polarity Solvent", *J. Am. Chem. Soc.*, (1994) 116, 9182-9186.
- 8) G. D Scholes, P. Matousek, A. W. Parker, D. Phillips, M. Towrie, "Inner sphere reorganization dynamics accompanying charge transfer in cyanoterphenyl", *J. Phys. Chem. A*, (1998) 102, 1431-1437.

9) W. M Kwok, C. Ma, P. Matousek, A. W. Parker, D Phillips, W. T. Toner, M. Towrie and S. Umaphy, "A determination of the structure of the intramolecular charge transfer state of 4 dimethylaminobenzonitrile (DMABN) by Time-resolved Resonance Raman Spectroscopy", *J. Phys. Chem. A*, (2001) 105, 984-990.

10) W. M. Kwok, M. George, D. C. Grills, C. S Ma, P. Matousek, A. W. Parker, D Phillips W. T. Toner and M. Towrie, "Direct observation of a hydrogen-bonded charge-transfer state of 4 dimethylaminobenzonitrile in methanol by time-resolved IR spectroscopy", *Angew. Chem-Int-Ed.*, (2003) 42, 1826-1830.

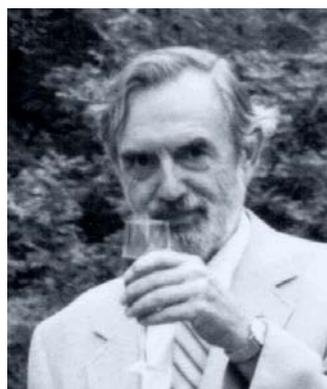
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Personal News

Obituary: Brian Stevens

Brian Stevens was born in Sheffield, England, on July 22, 1924. When he finished school in 1943 times were harder than nowadays. His country fought in World War II and demanded his contribution. The British Army sent him as a soldier to East Africa from where he returned after four years of service as Captain in 1947. Back home he started his studies of chemistry at Oxford University where he received an M.A. in 1950 and a D.Phil. in 1953, for his work on fluorescence quenching performed under the supervision of Prof. E. J. Bowen.



In the following two years he did research as a postdoctoral fellow at the NRC in Ottawa, Canada, from where he moved for two more years as a research associate to Princeton University. These positive experiences encouraged him to strive for an academic career. He returned to England in 1957 and took positions as Lecturer in Chemistry (until 1964) and as Reader in Photochemistry (until 1967) at Sheffield University.

During this time, Brian Stevens and his co-workers investigated the quenching and energy transfer processes of excited singlet and triplet state molecules in the vapour, liquid, and solid phase. He was particularly interested in the photophysics of aromatic compounds, in the kinetics of the formation and deactivation of excited dimers and in delayed fluorescence phenomena. During that first fruitful period, he published almost fifty articles, six of them in *Nature*. Brian Stevens was also a dedicated and excellent teacher as is documented by the books "Chemical Kinetics", "Atomic Structure and Valency", and "Collisional Activation in Gases" he wrote and which appeared during his time at Sheffield.

In 1967 Brian Stevens left England and went to the United States where he became Professor of Chemistry at the University of South Florida at Tampa. At this new position, he extended significantly his research on photoperoxidation reactions which he had already started in Sheffield. Using extensive reaction schemes he derived, with his brilliant analytical intellect, alarmingly complex appearing equations describing photoperoxidation quantum yields as functions of oxygen and substrate concentrations. It was actually amazing to experience Brian personally, when he easily drew with his fine calligraphic hand writing - like an artist - series of complicated equations on a sheet of paper. These elaborate kinetic equations proved to be very useful because they allow the determination of rate constants, sensitizer intersystem crossing and singlet oxygen sensitization efficiencies on the basis of appropriate stationary photochemical experiments.

During that second productive period Brian published a series of 25 publications on the photoperoxidation of unsaturated organic molecules. These works impressively demonstrate the depth he delved with his analysis into photoperoxidation consisting of numerous competing and subsequent reactions. On the basis of his important scientific contributions Brian Stevens was awarded a D.Sc. by Oxford University in 1977.

The binary complex of $O_2(^1\Delta_g)$ and ground state substrate molecule, named oxciplx by Stevens, may react to oxidation product or dissociate into the individual components, which both can reform the oxciplx with a certain re-encounter probability. That difficult to determine quantity is of principal interest for the understanding of molecular kinetics and diffusion. Brian Stevens realized that a very similar situation is given for a second excited species, namely the excimer, which may fluoresce or dissociate. Since both systems are suited to the determination of re-encounter probabilities, he studied the kinetics of oxciplexes and excimers in detail. The results on the solute re-encounter process were published in a series of seven articles written in the concise and clear style typical of him.

Beginning in 1984 Brian Stevens' scientific activity moved more in the direction of theoretical chemistry. In a series of eight papers, he investigated EDA complexes by means of Electron Donor Acceptor Orbital Correlations, where the influence of geometrical arrangement for the electron transfer was of particular interest.

From 1989 onwards, Brian Stevens was Graduate Research Professor at the USF at Tampa and retired ten years later in May 1999. He has been a major physical-chemist of his time, and his scientific contributions in several areas were crucial.

The most significant characteristics of his personality can be explained by his education that instilled in him the fundamental virtues of British "spirit" and by his commitment as Captain in the Army in East Africa and Ethiopia. There he learned Swahili, an African language, which enabled him to communicate with the Africans he met ... and amaze those present.

Brian Stevens had great wit and humour, sometimes rather caustic, but he could also be ironic with himself. Although courteous and pleasant, he was of reserved temperament, extremely shy of confidence and showed an apparent indifference to everything which appeared personal. This allowed him to stay upright, to keep his dignity and maintain the lifestyle he had chosen throughout his illness. But at the same time, he was warm and cordial, and sought to please others, by taking care of his guests and scientists working in his laboratory, or giving lots of time to his students. Moreover, his reliability, organizational skills and kindness during the many Conferences with which he had been involved have always been unanimously appraised.

In his private life Brian Stevens particularly enjoyed jazz music. He played the piano very well and was a fan of Duke Ellington and Hot Club de France. But golf was probably the passion of his life. With his indisputable natural elegance, combined with a high-level standard of behaviour, he was a brilliant scientist and a fine gentleman. It was a privilege and a pleasure to have known and worked with him. Brian Stevens passed away in the age of 85 on February 12, 2010.

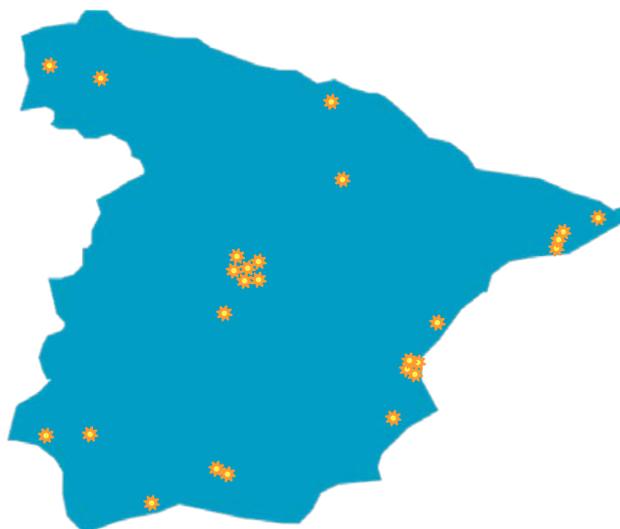
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ACTIVITIES OF NATIONAL GROUPS

Photochemistry in Spain

I have accepted the invitation to write a report for the EPA Newsletter on the present status of the active photochemistry groups in Spain. I apologize for any unintentional omissions. I thank my colleagues for their collaboration in sending the information regarding the composition of their groups, as well as their research activities and relevant recent publications, in a concise manner. During the preparation of this document I have realized how large the community of Spanish researchers is becoming. They are addressing experimental and theoretical studies related to the chemical and physical behaviour of electronically excited compounds. The variety of research lines is quite impressive, encompassing from theoretical to experimental investigation, using a wide range of systems, from inorganic materials to organic chromophores to biological systems, with applications from sensing, photocatalysis, drug toxicity determination, and pollution degradation. This research work is being performed using both conventional and more specialised techniques.



University of Alcalá de Henares
Centre: Faculty of Biology

Research Group: Dr. Obis Castaño; Dr. Luis Manuel Frutos; Dr. Raúl Palmeiro; Dr. Manuel Temprado; Dr. Gerardo Echevarría; Dr. José Luis Andrés; Marco Marazzi (PhD student); Unai Sancho (PhD student); Dr. José Kaneti (Visiting Professor); Sandra Acebes (Student).

Research Interests: the group is focused on the quantum chemical study of photoinduced processes in biological and chemical systems, using multiconfigurational methods for the study of photochemical and photophysical processes by exploring reaction paths, electronic state crossings (conical intersections and intersystem crossings, intersection and branching spaces) as well as dynamical properties by computing semiclassical dynamics. General topics of research are: photoinduced proton, electron and energy transfer in chemical and biological systems (proteins, DNA,...), as well photochemical reactions in photoactive proteins.

Special Techniques: Multi-configurational CASSCF and CASPT2 methods for determination of electronic structure. Hybrid Quantum Mechanics/Molecular Mechanics /QM/MM) for complex systems. Semiclassical dynamics in photoinduced processes.

Recent Publications:

1. M. Marazzi, U. Sancho, O. Castaño, W. Domcke, and L. M. Frutos. *J. Phys. Chem. Lett.* **2010**, *1*, 425
2. L. M. Frutos, U. Sancho, M. Garavelli, M. Olivucci, and O. Castaño. *J. Phys. Chem. A* **2007**, *111*, 2830
3. L. M. Frutos, A. Markmann, A. L. Sobolewski, and W. Domcke. *J. Phys. Chem. B*, **2007**, *111*, 6110
4. L. M. Frutos, T. Andruniów, F. Santoro, N. Ferré, and M. Olivucci. *PNAS*, **2007**, *104*, 7764
5. L. M. Frutos and O. Castaño. *J. Chem. Phys.* **2005**, *123*, 104

Autonomous University of Barcelona
Centre: Faculty of Chemistry

Research Group: Prof. José Luis Bourdelande; Prof. Iluminada Gallardo; Prof. Jordi Marquet; Dr. Gonzalo Guirado; Dr. Jordi

Hernando; Dr. Chao Liu; Dr. Claudio Roscini; Hugo Cruz; Gemma Prats; Rafael Sánchez; Marc Soto; Roser Gras; Enrique Moreno; Marta San Juan.

Research Interests: Synthesis and characterisation of photoactive materials (photo- and electro-triggered molecular switches, second-harmonic generator materials and photo-oxidative materials). Photochemical and electrochemical studies of Meisenheimer complexes in aromatic nucleophile substitution. Nanostructuring and characterization of photoactive materials on the nanoscale. Electrochemical studies of radicals and radical ions. Photoreduction of CO₂.

Special Techniques: Diffuse reflectance laser flash-photolysis. Confocal scanning fluorescence microscopy. Spectroelectrochemistry. Cyclic voltammetry

Recent Publications:

1. J.R. Herance, B. Ferrer, J.L. Bourdelande, J. Marquet, H. García, *Chem. Eur. J.*, **2006**, *12*, 3890.
2. R.O. Al-Kaysi, J.L. Bourdelande, I. Gallardo, G. Guirado, J. Hernando, *Chem. Eur. J.*, **2007**, *13*, 7066.
3. J.L. Bourdelande, I. Gallardo, G. Guirado, *J. Am. Chem. Soc.*, **2007**, *129*, 2817.
4. A. Martínez-Otero, E. Evangelio, R. Alibés, J.L. Bourdelande, D. Ruiz-Molina, F. Busqué, J. Hernando, *Langmuir*, **2008**, *24*, 2963.
5. I. Gallardo, G. Guirado, G. Prats, T. Michinori, *Phys. Chem. Chem. Phys.*, **2009**, *9*, 1502.

University of Barcelona

Centre: Faculty of Chemistry

Research Group: Prof. Santiago Esplugas (Head of the Group); Prof. Jaime Giménez; Prof. Esther Chamarro; Prof. Carme Sans; Dr. Renato Falcao; Dr. Óscar González; Paula Cajal; Angel Cruz; Natalia de la Cruz; Bruno Domenjoud; Marc Esplugas; Anna Justo; Pilar Marco; Fabiola Mendez; Mar Mico; Ywann Penru; Joao Pereira; Samanta Pereira; Violeta Romero; Bruno Santos

Research Interests: The objective of the research group is the application of Advanced oxidation processes (AOP) for water treatment and recovery. This includes many topics such as

wastewater and water treatment, water reuse, removal of emergent contaminants, etc.

At present, they are studying the combination of AOP and conventional biologic treatments in order to make pollutant degradation more economic. They use AOP in sewage aiming at water reuse, removal of organic matter in seawater, and removal of emergent pollutants in water.

Special Techniques: UV/hydrogen peroxide. Ozonation. Photo-Fenton (Solar). Titanium oxide photocatalysis. Combination of AOP and biological treatment for water purification.

Recent Publications:

1. S. Esplugas, D. Bila, G. Krause, M. Dezotti, *J. Hazard. Mat.*, **2007**, *149*, 631.
2. R. F. Dantas, M. Canterino, R. Marotta, C. Sans, S. Esplugas, R. Andreozzi, *Water Res.* **2007**, *41*, 2525.
3. B. Bayarri, M. N. Abellán, J. Giménez, S. Esplugas. *Catal. Today* **2007**, *129*, 231.
4. F. Méndez-Arriaga, R.A. Torres-Palma, C. Pétrier, S. Esplugas, J. Gimenez, C. Pulgarin. *Water Res.* **2009**, *43*, 3984.

University Ramon LLull, Barcelona
Centre: Chemistry Institute of Sarria

Research Group: Dr. Santi Nonell (Head of the Group), Dr. David Sánchez, Dr. Walter Massad, Roger Tejedor, Xavier Ragàs, María García-Díaz, Adaya Gallardo, Rubén Ruiz, Patricia López-Chicón, Roger Moltó.

Research Interests: The research carried out by this group can be generically described as the study of photosensitisation phenomena

and their applications in biology and medicine. The main interest of this research group is the development of novel photosensitisers for photodynamic therapy of cancer and infectious diseases. This has led them to develop the synthesis of porphycene macrocycles and to study the production, diffusion, and decay of the cytotoxic reactive oxygen species singlet molecular oxygen in biological media with time-resolved spectroscopic techniques developed in our laboratory. Using such techniques they have been able to characterise the kinetics of singlet oxygen in human skin fibroblasts, various cancer cell lines, and bacteria, and found that the kinetics of singlet oxygen production and decay can be used to establish the localisation of the photosensitiser in the cell, particularly useful for bacteria. More recently, they have conducted a study on mutants of the green fluorescent protein family as potential genetically-encoded photosensitisers.

Special Techniques: The laboratory is equipped with a nanosecond laser flash photolysis system with optical and optoacoustic detection lines. Optical detection of absorption and emission is available in the UV-Vis and NIR ranges. In addition, they also have a fluorescence lifetime system with picosecond time resolution with detectors covering the UV-Vis and NIR spectral ranges.

The laboratory has specialised in the technique of time-resolved singlet oxygen phosphorescence detection. They have a state-of-the-art time-resolved singlet oxygen spectroscopic detection facility developed in collaboration with the Picoquant company, that allows the detection of singlet oxygen through its phosphorescence at 1270 nm with unrivalled sensitivity and time resolution.

Recent Publications:

1. D.Sánchez-García, J.I. Borrell, S. Nonell, *Org. Lett.*, **2009**, *11*, 77
2. A. Jiménez-Banzo, X. Ragàs, P. Kapusta, S. Nonell, *Photochem. Photobiol. Sci.*, **2008**, *7*, 1003.
3. A. Jiménez-Banzo, M. L. Sagristá, M. Mora, S. Nonell, *Free Radical Biol. Med.*, **2008**, *44*, 1926.
- J.C. Stockert, M. Cañete, A. Juarranz, A. Villanueva, R. W. Horobin, J. I. Borrell, J. Teixidó, S. Nonell, *Curr. Med. Chem.*, **2007**, *14*, 997.
5. C. Flors, S. Nonell, *Acc. Chem. Res.*, **2006**, *39*, 293.

University Jaume I of Castellón
Centre: School of Technology and Experimental Science

Research Group: Santiago V. Luis (Head of the Group), Francisco Galindo, M. Isabel Burguete, M. Ángeles Izquierdo, Belén Altava, Eduardo García-Verdugo, Manuel Collado.

Research Interests: The research activity in the field of photochemistry at the University Jaume I in Castellón is carried out within the *Sustainable Chemistry Group* and deals with the following topics. Use of fluorescence techniques for the characterisation of new advanced materials obtained by self-assembly; synthesis of polymeric photosensitisers with application in both photocatalysis and photodynamic therapy; basic photochemical studies (photorearrangements); and synthesis of fluorescent sensors and their study in biomedical applications. In this regard, several molecular probes have been developed for the monitoring of species of biomedical interest, at the cellular level, like protons and nitric oxide.

Special Techniques: Steady-state and time-resolved (ns) fluorescence spectroscopy. Variable-temperature UV-vis absorption spectroscopy.

Recent Publications:

1. F. Galindo, M. I. Burguete, L. Vígara, S. V. Luis, N. Kabir, J. Gavrilovic, D. A. Russell, *Angew. Chem., Int. Ed.*, **2005**, *44*, 6504.
2. F. Galindo, N. Kabir, J. Gavrilovic, D. A. Russell, *Photochem. Photobiol. Sci.*, **2008**, *7*, 126 (journal cover, January).
3. M. I. Burguete, F. Galindo, R. Gavara, M. A. Izquierdo, J. C. Lima, S. V. Luis, A. J. Parola, F. Pina, *Langmuir*, **2008**, *24*, 9795.
4. M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci.*, **2009**, *8*, 37 (journal cover, January).
5. F. Galindo, The photochemical rearrangement of aromatic ethers. *J. Photochem. Photobiol. C: Photochemistry Reviews*, **2005**, *6*, 123.

University of Castilla-La Mancha
Centre: Faculty of Environmental Science

Research Group: Prof Abderrazzak Douhal (head of the group), Dr Juan Angel Organero, Dr Boiko Cohen, Dr Michal Gil, Dr Marcin Ziólek, Dr. Michal Zitnan, Dr Maria Rosaria di Nunzio, Cristina

Martin Alvarez (Ph.D Student) , Yilun Wang (Ph.D. student)
Roudaina Bouzaid (Ph..D. Student).

Research Interests: The group's investigations focus on the dynamical intra- and intermolecular processes occurring at ultrafast (femtoseconds to picoseconds) and slow (nanoseconds to seconds) regimes within chemically and biologically confined molecular systems. Time- and space-resolved studies carried out at both ensemble and single molecule level are also aimed towards designing and characterisation of new functional materials.

Special Techniques: Femtosecond emission up-conversion spectroscopy. Femtosecond transient absorption. Single molecule spectroscopy. Time-resolved (ns, ps) fluorescence; nanosecond flash photolysis.

Recent Publications:

1. B. Cohen, F. Sanchez, A. Douhal, *J. Am. Chem. Soc.*, **2010**, DOI. 10.1021/ja100771j.
2. B. Cohen, S. Wang, J. A. Organero, L. Franciscato Campo, F. Sanchez, A. Douhal, *J. Phys. Chem. C*, **2010**, DOI. 10.1021/jp911730u.
3. M. Gil, C. Martin, J. A. Organero, M. T. Navarro, A. Corma, A. Douhal, *J. Phys. Chem. C*, **2010**, DOI. 10.1021/jp911942d.
4. A. Synak, M. Gil, J. A. Organero, F. Sanchez, M. Iglesias, A. Douhal, *J. Phys. Chem. C*, **2009**, *113*, 19199.
5. M. Gil, S. Wang, J. A. Organero, L. Teruel, H. Garcia, A. Douhal, *J. Phys. Chem. C*, **2009**, *113*, 11614.

University of Girona

Centre: Institute of Computational Chemistry

Research Group: Dr. Lluís Blancafort (Head of the Group), Dr. Quansong Li, Dr. Sergi Ruiz.

Research Interests: Computation of excited state processes, with a special interest in the role of conical intersections in molecular photochemistry and photophysics. The group is focussing on applications of biological and technological relevance, such as the

photophysics and photochemistry of the DNA nucleobases or excited-state hydrogen transfer in model photoprotectors. These processes are studied with quantum chemistry methods, including the calculation of potential energy surfaces and non-adiabatic dynamics. They also develop methods for the analysis of conical intersections.

Special Techniques: Multireference *ab initio* methods; second-order analysis of conical intersection topographies; semiclassical dynamics (trajectory surface hopping).

Recent Publications:

1. D. Asturiol, B. Lasorne, M. A. Robb, L. Blancafort, *J. Phys. Chem. A* **2009**, *113*, 10211-10218.
2. A. Migani, L. Blancafort, M. A. Robb, A. D. DeBellis, *J. Am. Chem. Soc.* **2008**, *130*, 6932-6933.
3. F. Sicilia, L. Blancafort, M. J. Bearpark, M. A. Robb, *J. Chem. Theory Comput.* **2008**, *4*, 257-266.
4. L. Blancafort, A. Migani, *J. Am. Chem. Soc.* **2007**, *129*, 14540-14541.
5. F. Sicilia, L. Blancafort, M. J. Bearpark, M. A. Robb, *J. Phys. Chem. A* **2007**, *111*, 2182-2192.

University of Granada

Centre: Faculty of Pharmacy, Group of Photochemistry and Photobiology

Research Group: Dr. José M^a Álvarez Pez (Head of the Group); Dr. Eva M^a Talavera Rodríguez, Dr. M^a Carmen del Valle Ribes, Dr. Luis Crovetto González, Dr. Ángel Orte Gutiérrez, Dr. M^a José Ruedas Rama, Dr. José Manuel Paredes Martínez, Patricia Lozano Vélez, Sofía Victoria Cervilla Sánchez.

Research Interests: DNA fluorescent probes. Synthesis of new fluorescein derivatives and study of their photophysical behaviour. Reactions of proton transfer in the excited state. Förster resonance energy transfer (FRET) between dyes and DNA intercalators. Photophysical study of fluorophores at the single-molecule level and fluorescence correlation spectroscopy. Single-molecule fluorescence spectroscopy for the study of protein interactions.

Special Techniques: Confocal fluorescence microscopy

Recent Publications:

1. L. Crovetto, J. M. Paredes; R. Rios; E. M. Talavera, J. M. Alvarez-Pez. *J. Phys. Chem. A* **2007**, *111*, 13311.

2. L. Crovetto, R. Rios, J. M. Alvarez-Pez, J. M. Paredes, P. Lozano-Velez, C. del Valle, E. M. Talavera, *J. Phys. Chem. B* **2008**, *112*, 10082.
3. J. M. Paredes; L. Crovetto, R. Rios, A. Orte, J. M. Alvarez-Pez, E. M. Talavera. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5400.
4. M. J. Ruedas-Rama, A. Orte, L. Crovetto, E. M. Talavera, J. M. Alvarez-Pez. *J. Phys. Chem. B* **2010**, *114*, 1094.
5. J. M. Paredes, A. Orte, L. Crovetto, J. M. Alvarez-Pez, R. Rios, M. J. Ruedas-Rama, E. M. Talavera. *Phys. Chem. Chem. Phys.* **2010**, *12*, 323.

Centre: Faculty of Pharmacy, Group of Pharmaceutical Physical Chemistry

Research Group: Bartolomé Quintero Osso (Head of the Group); María del Carmen Cabeza González; María Isabel Martínez Puentedura; Pedro J Martínez de las Parras

Research Interests: Chemical physics studies on potential inhibitors of Zn-dependent β -lactamases. Metallic complexes of penamaldic derivatives. Kinetic studies of the inhibition processes by fluorescence spectroscopy. Thermal and photochemical reactions of free radical precursors. Mechanism of the decomposition of arenediazonium ions. Design and characterisation of systems based on quantum points for the detection and characterisation of Cu(II) ions in critically ill patients.

Recent Publications:

1. P. Gutierrez, B. Quintero, R. García, P.J. Martínez, M. I. Martínez, M. C. Cabeza, *Antimicrob Agents Chemother.*, **2004**, *48*, 1058.
2. B. Quintero, E. Planelles, M. C. Cabeza, J. Esquivias M. P. Gutiérrez, C. Sánchez, P. Aranda, A. Zarzuelo, J. Llopis, *J. Chem. Biol. Interact.*, **2006**, *159*, 186.
3. B. Quintero, M. C. Cabeza, A. el Bekkouri, P. Ros, *Luminescence*, **2006**, *21*, 363.
4. E. Planelles, M Rodríguez Elvira, J. Castaño, A. Pérez de la Cruz, B. Quintero, J. Llopis, C. Sánchez, E. Millán, J. Abides, D. Florea, M. García-Ávila, M. C. Cabeza, R. Romero Torres P. Aranda, *Clin. Nutr. Supplements*, **2008**, *3*, 113.

University of Huelva
Centre: Faculty of Experimental Sciences

Research Group: Dr. Uwe Pischel (Head of the Group); Patricia Remón (PhD Student); Vânia Pais (PhD Student); Cátia Carvalho (PhD Student)

Research Interests: Design, synthesis, and photophysical characterisation of fluorescent compounds for application as molecular logic devices and memories, fluorescent chemosensors/assays for compounds of biological importance (anions, enzymes, nucleic acids, etc.). Supramolecular host-guest complexes with fluorescent guests. Photoactive nanomaterials (ligand-functionalised nanoparticles and quantum dots). Study of electronic energy transfer in bichromophoric model compounds and photochromic switches.

Special Techniques: Steady-state and time-resolved fluorescence (TCSPC). Transmission electron microscopy

Recent Publications:

1. S. Abad, M. Kluciar, M. A. Miranda, U. Pischel, *J. Org. Chem.*, **2005**, *70*, 10565.
2. M. de Sousa, B. de Castro, S. Abad, M. A. Miranda, U. Pischel, *Chem. Commun.*, **2006**, 2051.
3. A. L. Koner, J. Schatz, W. M. Nau, U. Pischel, *J. Org. Chem.*, **2007**, *72*, 3889.
4. R. Ferreira, P. Remón, U. Pischel, *J. Phys. Chem. C*, **2009**, *113*, 5805.
5. U. Pischel, *Angew. Chem. Int. Ed.*, **2010**, *49*, 1356.

University of La Rioja
Centre: Faculty of Science

Research Group: Prof. Dr. Pedro J. Campos (Head of the Group); Prof. Dr. Miguel A. Rodríguez; Dr. Diego Sampedro; Dr. Laura Rivado; Alegría Caballero; Marina Blanco; Héctor F. González (PhD student).

Research Lines: Photochemistry of imines and azadienes. Photochemical reactivity of metallocarbenes and other organometallic species. Synthesis of polycyclic structures via photocyclisation of species with N-O bonds. Studies of vinylcyclopropane-cyclopentene rearrangements and analogue reactions. Synthesis and

characterisation of biomimetic molecular switches. Computational studies of organometallic reactions. Computational studies of photochemical reactions. Photo-curing resins.

Special equipment: Laser Flash Photolysis (ns); fluorolog spectrophotometer model Jovin-Yvon Horiba 3-22 Tau3. Computational photochemistry (Gaussian 03, Molcas 5.4 y 6 programs)

Research Publications:

1. D. Sampedro, A. Soldevilla, M.A. Rodríguez, P.J. Campos, M. Olivucci, *J. Amer. Chem. Soc.* **2005**, *127*, 441.
2. R. Alonso, P. J. Campos, B. García, M. A. Rodríguez, *Org. Lett.* **2006**, *8*, 3521.
3. R. Alonso, P. J. Campos, M. A. Rodríguez, D. Sampedro, *J. Org.Chem.* **2008**, *73*, 2234.
4. D. Sampedro, A. Soldevilla, P. J. Campos, R. Ruiz, M. A. Rodríguez, *J. Org.Chem.* **2008**, *73*, 8331-8336.
5. L. Rivado-Casas, D. Sampedro, P. J. Campos, S. Fusi, V. Zanirato, M. Olivucci, *J. Org.Chem.* **2009**, *74*, 4666.

Spanish National Research Council (CSIC)-Madrid

***Centre: Institute of Physical Chemistry "Rocasolano",
Department of Laser Chemistry***

Research Group: Prof. Angel Costela (Head of the Group); Dr. Inmaculada García-Moreno, Dr. Clara Gómez, Dr. Virginia Martín, Luis Cerdán, M^a Eugebia Pérez.

Research Interests: Design and synthesis of new organic dyes for solid-state dye lasers and photodynamic therapy. Photosensitised materials for solid-state dye lasers. Nanostructures for advanced optics and biophotonics. Relationship between structure-composition and photophysical, photochemical, and optical properties.

Special Techniques: Optical spectroscopies: LIF (Laser Induced Fluorescence), LIBS (Laser Induced Breakdown Spectroscopy), optical emission multiphotonic, and pump and probe spectroscopies. Pulsed laser ablation. Non linear optical techniques (phase conjugation and harmonic generation). Photoacoustic techniques.

Special Equipment: Laser equipment: excimer lasers (XeCl 308 nm), Nd:YAG lasers with stages for harmonic generation up to the 3rd harmonic (1064, 532, 355); dye laser (oscillator and two amplifiers

pumped with the third harmonic of Nd:YAG, with emission from the blue to the red); He-Ne lasers. Equipment for dispersion and detection of light: monochromators/spectrographs, photomultipliers, CCD detectors, photodiodes. Equipment for the acquisition and treatment of signal and data: boxcar integrators, oscilloscopes, interphases, computers. Auxiliary equipment: delayed pulse generators, power supplies, energy and power meters.

1. A. Costela, I. García-Moreno, M. Pintado-Sierra, F. Amat-Guerri, R. Sastre, F. López, I. Arbeloa, J. Bañuelos Prieto, and I. López Arbeloa, *J. Phys. Chem. A* **2009**, *113*, 8118.
2. I. García-Moreno, A. Costela, V. Martín, M. Pintado-Sierra, and R. Sastre, *Adv. Funct. Mater.* **2009**, *19*, 2547.
3. L. Cerdán, A. Costela, I. García-Moreno, O. García, and R. Sastre, *Appl. Phys. B*, **2009**, *97*, 73.
4. A. Costela, I. García-Moreno, L. Cerdán, V. Martín, O. García, and R. Sastre, *Adv. Mater.* **2009**, *21*, 4163.
5. R. Sastre, V. Martín, L. Garrido, J.L. Chiara, B. Trastoy, O. García, A. Costela, and I. García-Moreno, *Adv. Funct. Mater.* **2009**, *19*, 3307.

***Centre: Institute of Physical Chemistry "Rocasolano",
Department of Biophysics***

Research Group: Dr. A. Ulises Acuña, Dr. Pilar Lillo, Dr. Carolina García, Dr. Silvia Zorrilla

Research lines: The research activity of the group is concerned with the development and application of time-resolved fluorescence spectroscopy methods to the study of the relationship between structure, dynamics and function of bio-molecules, in solution, model systems and at the single-cell level. They develop fluorescent analogues of anti-tumour or anti-parasite drugs which make it possible to detect therapeutic targets of the drug using fluorescence microscopy. These emitting and bioactive analogues are used to investigate the mechanism of action of the drug at the molecular level, both in cells and unicellular organisms. Moreover, the group uses other fluorescent molecular probes, labelled proteins and nucleic acids and genetically modified yeasts expressing fluorescent proteins to understand basic biological processes or the effect of compounds with pharmaceutical interest. Fundamental research is also carried out

in the field of T-T energy transfer and on the chemical history of fluorescence.

Special Techniques: Pico-second multi-wavelength laser spectrometer for the determination of fluorescence and anisotropy decay times of samples in solution. Wide-field and confocal two-photon fluorescence microscopes, with FCS, lifetime and anisotropy recording capabilities.

1. V. Hornillos, Carrillo, E., Rivas, L., Amat-Guerri, F., Acuña, A.U., *Org. Lett.* **2008**, 18, 6336.
2. E. Quesada, J. Delgado, V. Hornillos, A. U. Acuña, F. Amat-Guerri, *Eur. J. Org. Chem.* **2007**, 2285.
3. A. Coutinho, C. García, J. González-Rodríguez, M. P. Lillo, *Biophys. Chem.* **2007**, 130, 76.
4. S. Zorrilla, B. Garzón, D. Pérez-Sala, *Analytical Biochem.* **2010**, 399, 84.
5. A.U. Acuña, F. Amat-Guerri, P. Morcillo, M. Liras, B. Rodríguez, *Org. Lett.* **2009**, 11, 3020.

Centre: Institute of Polymer Science and Technology

Research Group: Fernando Catalina, Paula Bosch, Carmen Peinado, Teresa Corrales

Research Interests: *Study of environmental degradation process and polymer stabilisation:* The research is focused on obtaining photoselective, photodegradable and biodegradable agricultural films, through the incorporation of specific additives. Study of polyolefin stabilisation, through the addition of new stabilisers. Study of polymer degradation particularly using chemiluminescence. *Fluorescent Probes:* Synthesis of novel organic compounds and highly fluorescent polymeric structures. Synthesis of “antenna” dendrimers. Evaluation of environmental pollutants, organic acids and metallic salts as target chemicals. Study of processes in polymers: cross-linking reactions, photo-curing of adhesives, thermal transitions in polymers, transport of molecules, carbohydrates-DNA binding. *Novel polymer materials obtained by photopolymerisation reactions and using controlled radical polymerisation:* Preparation of photocurable nanocomposites, microparticles, mesoporous solids and cross-linked coatings through hyperbranched polymers. Study of the properties of such systems. Preparation of photocurable organo-silicate based nanocomposites.

Study of reaction kinetics via photo-DSC. XRD, TGA, SEM nanomaterial characterisation. Study of thermo-oxidative processes. Preparation of block-copolymers. Study of order-desorder transitions. Study of auto-assembly and auto-organisation by different techniques (fluorescence, SEM and AFM microscopy). Application in controlled dosage and micelle-improved ultra-filtration.

Special Techniques: Lasers (Pulsed Laser System Nd-YAG Spectra Physics INDI. /ICCD Camera) and environmental photo-ageing systems (ATLAS-Xe-Lamp and QUV-fluorescence lamps). Chemiluminescence ATLAS CL-400

Recent Publications:

1. T. Corrales, M. Escudero, R. Quijada, F. Catalina, C. Abrusci, *Eur. Polymer, J.* **2009**, *45*, 2708.
 2. V. San Miguel, F. Catalina, C. Peinado, *Eur. Polym. J.*, **2008**, *44*, 1368.
 3. P. Bosch, C. Peinado, V. Martín, F. Catalina, T. Corrales, *J. Photochem. Photobiol., A: Chem.*, **2006**, *180*, 118.
- P. Bosch, A. Fernández, E.F. Salvador, T. Corrales, F. Catalina, C. Peinado, *Polymer*, 2005, 46, 12200.**
4. P. Bosch F. Catalina, T. Corrales, C. Peinado, *Chem. Eur. J.*, **2005**, *11*, 1.

The Complutense University of Madrid (UCM)

Centre: Faculty of Chemistry, Chemical Optosensors & Applied Photochemistry Group

Research Group: Prof. Guillermo Orellana (Head of the group), Prof. María C. Moreno-Bondi, Prof. David García-Fresnadillo, Prof. Concepción Pérez-Conde, Prof. Ana M. Gutiérrez, Prof. María D. Marazuela, Prof. Josefa Isasi, Prof. Gonzalo F. Colmenarejo, Dr. Fernando Navarro-Villoslada, Dr. Juan López-Gejo, Dr. Clara Cano, Dr. Manoel Veiga, Dr. Ana B. Descalzo, Francisco Manjón, André R. Santos, Silvia Mateos, Erika Rodríguez-Carvalho, David Haigh, Sonia Herranz, Jolanta Zdunek, Klécia Morais, Zhen-He Chen, Markel D. Luaces.

Research Interests: Development of fiber-optical sensors and biosensors for in situ, real time, continuous monitoring of chemical species in the environment or industrially waste based on photochemical/photophysical processes. Molecular engineering,

synthesis and photochemical characterisation of indicator dyes for chemical sensing. Molecularly imprinted polymers with signalling features for optical sensors and optical methods of analysis development. Tailored luminescent labels for quality control, security tagging and molecular biology (nucleic acids, proteins and whole cells). Photodynamic action for solar-powered water treatment.

Special Techniques: Nanosecond laser flash photolysis and kinetic spectrometry in the UV-VIS-NIR range for solutions and in diffuse-reflectance mode. Confocal fluorescence lifetime imaging microscopy using single-photon timing (FLIM-SPT). Sub-ns single photon timing in solution and in the solid state. Luminescence lifetime measurements with phase-sensitive detection in the sub-microsecond and microsecond range.

Recent Publications:

- E. Benito-Peña, M.C. Moreno-Bondi, S. Aparicio, G. Orellana, J. Cederfur, M. Kempe, *Anal. Chem.* **2006**, *78*, 2019.
- F. Manjón, L. Villén, D. García-Fresnadillo, G. Orellana, *Environmental Sci. & Technol.* **2008**, *42*, 301.
- F. Manjón, D. García-Fresnadillo, G. Orellana, *Photochem. Photobiol. Sci.* **2009**, *8*, 926.
- J. López-Gejo, D. Haigh, G. Orellana, *Langmuir* **2010**, *26*, 2144.
- J. López-Gejo, A. Arranz, A. Navarro, C. Palacio, E. Muñoz y G. Orellana, *J. Am. Chem. Soc.* **2010**, *132*, 1746.

Centre: Faculty of Chemistry, Group of Application of Photochemistry in Organic Synthesis.

Research Group: Prof. Diego Armesto Vilas; Dr. M^a José Ortiz García; Dr. Antonia Rodríguez Agarrabeitia. Gonzalo Durán Sampedro (collaboration with CSIC).

Research Interests: Photochemical reactivity of 1,4- and 1,5-unsaturated compounds promoted by triplet photosensitisers and electron transfer photosensitisers. Design and synthesis of new dyes derived from dipyrromethane-BF₂ (BODIPY's) and boraazaanthracenes (BTAA) for different applications (lasers in the solid state, photodynamic therapy). Design and synthesis of new dipyrromethene dyes.

Recent Publications:

1. D. Armesto, M. J. Ortiz, A. R. Agarrabeitia and M. Martín-Fontecha, *Org. Lett.* **2004**, *6*, 2261.

2. D. Armesto, M. J. Ortiz, A. R. Agarrabeitia and M. Martín-Fontecha, *Org. Lett.* **2005**, *7* (13), 2687.
3. D. Armesto, M. J. Ortiz, A. R. Agarrabeitia and N. El-Boulifi, *Angew. Chem. Int. Edit.* **2005**, *44*, 7739.
4. D. Armesto, M. J. Ortiz, A. R. Agarrabeitia, M. Martín-Fontecha, N. El-Boulifi, G. Durán-Sampedro, D. Emma, *Org. Lett.* **2009**, *11*, 4148.
5. M. J. Ortiz, I. Garcia-Moreno, A. R. Agarrabeitia, G. Durán-Sampedro, A. Costela, R. Sastre, F. López Arbeloa, J. Bañuelos Prieto, I. López Arbeloa, *Phys. Chem. Chem. Phys.* 2010, DOI: 10.1039/B925561C.

University of Málaga
Centre: Faculty of Science

Research Group: Ezequiel Pérez-Inestrosa; Rafael Suau; Francisco Nájera; Daniel Collado; Yolanda Vida.

Research Interests: Isolation, characterisation, synthesis, biosynthesis, and pharmacological activity of berbine, protopine, cularine, aporphine, and bencilisoquinoline alkaloids. Synthetic applications and organic photochemistry mechanistic aspect of phtalimides, benzyl phenyl and phenolic esters, and supramolecular systems. Molecules integrating photoresponsive logic circuits. Natural product-inspired photonic logic gates.

Recent Publications:

1. P. Remón, R. Ferreira, J-M Montenegro, R. Suau, E. Pérez-Inestrosa, U. Pischel. *ChemPhysChem*, **2009**, *10*, 2004.
2. E. Perez-Inestrosa, J-M. Montenegro, D. Collado, R. Suau. *Chem. Comm.*, **2008**, 1085.
3. E. Perez-Inestrosa, J. M. Montenegro, D. Collado, R. Suau, J. Casado. *J. Phys. Chem. C*, **2007**, *111*, 6904.
4. Y. Vida, R. Suau, J. Casado, A. Berlin, J. T. López Navarrete, E. Pérez-Inestrosa. *Macromol. Rapid Commun.* **2007**, *28*, 1345.
5. J. M. Montenegro, E. Pérez-Inestrosa, D. Collado, Y. Vida, R. Suau. *Organic Lett.*, **2004**, *6*, 2353.

University of Santiago de Compostela
Centre: Faculty of Chemistry

Research Group: Manuel Mosquera González; José Luis Pérez Lustres; M^a Carmen Ríos Rodríguez; Flor Rodríguez Prieto.

Research Interests: Dynamics of solvation processes and photochemical reactions. Kinetics of photoinduced proton- and electron-transfer processes. Ultrafast signal transduction in biological photoreceptors. Photophysical characterisation of new materials and fluorescent probes. Fluorescence spectroscopy and ultrafast optical spectroscopy.

Special Techniques: Steady-state and time-resolved fluorescence techniques. Transient absorption spectroscopic techniques.

Recent Publications:

1. A. Brenlla, F. Rodríguez-Prieto, M. Mosquera, M. A. Ríos, and M. C. Ríos Rodríguez, *J. Phys. Chem. A* **2009**, *113*, 56.
2. S. Ríos Vázquez, M. C. Ríos Rodríguez, M. Mosquera, and F. Rodríguez-Prieto, *J. Phys. Chem. A* **2008**, *112*, 376.
3. J. L. Pérez-Lustres, F. Rodríguez-Prieto, M. Mosquera, T. A. Senyushkina, N. P. Ernsting, and S. A. Kovalenko, *J. Am. Chem. Soc.* **2007**, *129*, 5408.
4. J. L. Pérez Lustres, A. L. Dobryakov, A. Holzwarth, and M. Veiga, *Angew. Chem. Int. Ed.* **2007**, *46*, 3758.
5. R. J. Brea, M. E. Vázquez, M. Mosquera, L. Castedo, and J. R. Granja, *J. Am. Chem. Soc.* **2007**, *129*, 1653.

Centre: Faculty of Sciences, Campus of Lugo.

Research Group: Prof. Dr. Mercedes Novo Rodríguez, Prof. Dr. Wajih Al-Soufi, Jorge Bordello Malde, Carlos Carreira Blanco, Sonia Freire Rodríguez, Daniel Granadero Rey, Lucas Piñeiro Maseda

Research lines: The principal aim of the research group is to exploit the unique features of single-molecule fluorescence detection for the study of host-guest association and molecular self-assembly in different supramolecular systems of biomedical and technological interest. Using as a springboard the intrinsic advantages of single-molecule techniques, the group aim is obtaining kinetic and structural information, not easily accessible by other methodologies.

Special Techniques: Steady state and time resolved fluorescence spectroscopy, fluorescence correlation spectroscopy (FCS), multiparametric single molecule fluorescence detection (SMFD).

Recent Publications:

1. D. Granadero, J. Bordello, M. J. Pérez-Alvite, M. Novo, Mercedes; W. Al Soufi, *Int. J. Mol. Sci.* **2010**, *11*, 173.
2. J. Bordello, B. Reija, W. Al-Soufi, M. Novo, *ChemPhysChem*, **2009**, *10*, 931.
3. W. Al-Soufi, B. Reija, S. Felekyan, C. A. Seidel, M. Novo, *ChemPhysChem* **2008**, *9*, 1819.
4. M. Novo, S. Felekyan, C. A. M. Seidel, W. Al-Soufi, *J. Phys. Chem. B*, **2007**, *111*, 3614.
5. W. Al-Soufi, B. Reija, M. Novo, S. Felekyan, R. Künemuth, C. A. M. Seidel. *J. Am. Chem. Soc.* **2005**, *127*, 8775.

University of Sevilla

Centre: Faculty of Pharmacy

Research Group: Prof. Dr. Manuel Balón Almeida (Head of the Group); María Asunción Muñoz Pérez; Carmen Carmona Guzmán; José Hidalgo Toledo; Antonio Sánchez Coronilla; Emilio García Fernández.

Research Interests: Physical properties of carbolines and diaza-aromatic betacarbolines. Photoinduced hydrogen-bond interactions and proton transfer reactions. Phototautomerism.

Special Techniques: Time-resolved (pico- and nano-second) fluorescent spectroscopy. Time-correlated photon counting.

Recent Publications:

1. C. Carmona, M. Balón, A. Sánchez-Coronilla, M.A. Muñoz, *J. Phys. Chem. A*, **2004**, *108*, 1910.
2. M. A. Muñoz, C. Carmona, M. Balón, *Chem. Phys. Lett.* **2004**, *393*, 217.
3. A. Sánchez-Coronilla, M. Balón, M.A. Muñoz, J. Hidalgo, C. Carmona, *Chem. Phys.* **2008**, *351*, 27.
4. J. Hidalgo, A. Sánchez-Coronilla, M. Balón, M.A. Muñoz, C. Carmona, *Photochem. Photobiol. Sci.*, **2009**, *8*, 414.
5. A. Sánchez-Coronilla, M. Balón, E. Sánchez Marcos, M. A. Muñoz, C. Carmona, *Phys. Chem. Chem. Phys.*, *2010*, **DOI: [10.1039/b923284b](https://doi.org/10.1039/b923284b)**

Polytechnic University of Valencia-CSIC Valencia
Centre: Department of Chemistry /Institute of Chemical
Tecnology UPV-CSIC.
Photochemistry and Photobiology Group

Research Group: Prof. Dr. Miguel A. Miranda (Head of the Group); Dr. M. C. Jiménez, Dr. M. L. Marín, Dr. I. M. Morera, Dr. R. Tormos; Dr. R. Alonso, Dr. I. Andreu, Dr. M. C. Cuquerella, Dr. V. Lhiaubet-Vallet, Dr. R. Pérez-Ruiz, Dr. G. Rodríguez, Dr. A. Sánchez; P. Bonancia, P. Bartovsky, M. Gómez, M. Marín, G. Nardi, E. Nuin, S. Soldevilla, J. Rohacova.

Research Interests: *Photosensitised electron transfer:* Pyrylium salts are powerful photosensitisers with synthetic applicability. Their tunable excited-state oxidising potential and multiplicity allows controlling the reaction selectivity. 2,4,6-Triphenylpyrylium, synthesised inside the supercages of zeolite Y, exhibits unique properties (enhanced charge separation, retardation of back electron transfer, restricted diffusion, increased cage effect). *Chiral recognition in the excited-states:* Time-resolved spectroscopy provides direct experimental evidence for remarkable stereodifferentiation in various photoprocesses (hydrogen abstraction, exciplex formation, electron transfer or energy transfer). Chiral excited states have also been used as probes for the microenvironments of biomacromolecules. The triplet lifetimes dramatically depend on the nature of the binding sites and are highly sensitive to the stereochemistry of the chiral chromophores. A remarkable stereodifferentiation has been found within human serum albumin. Recent applications of this concept deal with determination of enantiomeric compositions or *in situ* monitoring of the glucuronidase activity of proteins. *Photosensitisation by drugs:* The photophysical and photochemical aspects of photosensitisation by drugs have been disclosed. Studies on the interaction between drug excited states and biomolecules provide clear evidence for substrate-dependent oxidative lesions. At cellular level, damage to the membranes and the nuclei is observed. Covalent drug-protein photobinding (relevant to photoallergy) is detected by using radiolabelling and drug-directed antibodies. A recent breakthrough has been determination of the triplet energy of thymine in DNA, a critical parameter for photogenotoxicity.

Special Techniques: Steady-state and time-resolved fluorescence. Nanosecond laser flash photolysis. Tandem MS coupled with UPLC (Q-TOF). Oligonucleotide sensitiser.

Recent Publications:

1. C. J. Bueno, M. C. Jiménez, M. A. Miranda, *J. Phys. Chem. B*, **2009**, *113*, 6861.
2. I. Vayá, C. J. Bueno, M. C. Jiménez, M. A. Miranda, *Chem. Eur. J.* **2008**, *14*, 11284.
3. C. Paris, S. Encinas, N. Belmadoui, M. J. Climent, M. A. Miranda, *Org. Lett.* **2008**, *10*, 4409.
4. S. Abad, F. Bosca, L. R. Domingo, S. Gil, U. Pischel, M. A. Miranda, *J. Am. Chem. Soc.* **2007**, *129*, 7407.
5. F. Bosca, V. Lhiaubet-Vallet, M. C. Cuquerella, J. V. Castell, M. A. Miranda, *J. Am. Chem. Soc.* **2006**, *128*, 6318.

Centre: Department of Chemistry /Institute of Chemical Technology UPV-CSIC.

Research Group: Prof. Dr. Hermenegildo García (Group Leader), Dr. Mercedes Alvaro; Dr. Belen Ferrer; Amarajothi Dhakshinamoorthy; Roberto Martín; Maykel de Miguel; Marco Serra.

Research Interests: Photochemistry as a tool for solving environmental problems and preparation of solar cells. Organic photochemistry within zeolites and the use of zeolites as heterogeneous photocatalysts for organic reactions. Preparation of photo and electroactive systems encapsulated within zeolites. Development of photoactive nanoscopic materials and heterogeneous catalysis.

Relevant techniques: diffuse reflectance laser flash photolysis.

Recent Publications

1. P. Montes-Navajas, H. Garcia, *J. Phys. Chem. C* **2010**, *114*, 2034.
2. L. Teruel, Y. Bouizi, P. Atienzar, V. Fornes, H. Garcia, *H. Energy Envir. Sci.* **2010**, *3* 154.
3. C. G. Silva, Y. Bouizi, V. Fornes, H. Garcia, *J. Am. Chem. Soc.* **2009**, *131*, 13833.
4. M. Alvaro, C. Aprile, B. Ferrer, F. Sastre, F., H. Garcia, *Dalton Trans.* **2009**, 7437.
5. R. Martin, L. B. Jimenez, M. Alvaro, J. C. Scaiano, H. Garcia, *Chem. Eur. J.* **2009**, *15*, 8751.

Centre: Polytechnic University of Valencia, Campus of Alcoy.

Research Group: Ana M^a Amat Payá (Group Leader), Antonio Arques Sanz; Alicia Domenech Miró; Jaime Pey Clemente; Rosa F. Vercher Pérez; Rafael Vicente Candela; Antonio Bernabeu García; Juan Soler Escoda; Juan Gomis; Lorena Sanjuán

Research Interests: The group has different research lines, dealing in all cases with the use of advanced oxidation processes, and solar photocatalysis in particular, to detoxify wastewaters: Use of solar photocatalysis (photo-Fenton and TiO₂) to treat different industrial wastewaters (paper industry, textile industry, metal finishing, spray booths effluents...); use of solar photocatalysis to remove persistent compounds, such as pesticides, or emerging pollutants; improvement of quality of natural waters by means of solar processes; study of analytical methods to determine changes in biodegradability/toxicity to couple solar photocatalysis with biological treatments; development of organic photocatalysts able to use sunlight more efficiently.

Relevant Techniques: This group has a considerable experience in wastewater treatment. This work is carried out at the laboratory of the Group of Advanced Oxidation Processes of the Technical University of Valencia (UPV), which is located at the Carbonell building at the Campus of Alcoy of the UPV. In particular, the Chemistry laboratory is used for routine purposes. The laboratory of chemical analysis is equipped with different chromatographic techniques (HPLC, UPLC, GC-MS, IC), conventional spectroscopic methods, a total organic carbon analyzer for liquid and solid samples (which is also able to analyze total nitrogen), different selective electrodes, a tensiometer and equipment for SPE extraction and sample preparation. Finally, the laboratory of environmental chemistry is prepared to test different advanced oxidation processes: plants for solar detoxification of effluents based on CPC technologies, solar simulators, an ozone generator and reactor for ozonation, lamps and reactors for UV-C treatments, and a plant for electrochemical treatment. It is also equipped with different techniques to monitor toxicity and biodegradability of treated effluents, such as COD, BOD₅, electrolytic and activated sludge respirometers, luminometers to measure inhibition of luminescent bacteria.

Recent Publications:

1. J. Soler, A. García-Ripoll, N. Hayek, R. Vicente, A. Arques, A. M. Amat, *Water Res.* **2009**, *43*, 4441.
2. M. L. Dell'Arciprete, L. Santos-Juanes, A. Arques, R. Vicente, A. M. Amat, J. P. Furlog, D. O. Mártire, M. C. Gonzalez, *Photochem. Photobiol. Sci.*, **2009**, *8*, 1016.

3. A. M. Amat, A. Arques, F Galindo, M. A. Miranda, L. Santos-Juanes, R. F. Verchet, R. Vicente, *Applied Catal. B*, **2007**, *73*, 220.
4. A. M. Amat, A. Arques, S. H. Bossmann, A. M. Braun, S. Göb, M. A. Miranda, *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 1653.
5. M. A. Miranda A. M. Amat, A. Arques, M. L. Marín, S. Seguí S., *Applied Catal. B*, **2002**, *35*, 167.

University of Valencia

Centre: Molecular Science Institute. Group of Quantum Chemistry of the Excited State

Research Group: Prof. Dr. Manuela Merchán (Head of the Group); Dr. Remedios González-Luque; Dr. Luis Serrano-Andrés; Dr. Mercedes Rubio; Dr. Pedro B. Coto; Dr. João Paulo Gobbo; Dr. Juan José Serrano-Pérez; Dr. Daniel Roca-Sanjuán; Dr. Gloria Olaso-González; Teresa Climent; Israel Alberto González-Ramírez; Vicenta Saurí; Angelo Giussani; Javier Segarra Martí; Vicente Pérez Mondejar

Research Interests: The group of Quantum Chemistry of the Excited State group of the Molecular Science Institute of the University of Valencia (QCEXVal), Spain, focuses its research in the theoretical study of photoinduced molecular process using quantum chemistry methods. In particular we develop and apply ab initio quantum chemical multiconfigurational procedures in the determination of the molecular basis of photochemical reactions studying potential energy surfaces and molecular properties in electronic excited states, including studies on photophysics and nonadiabatic processes through conical intersections, electron and energy transfer, and proton and hydrogen transfer. The group main interest concentrates on studies of biologically relevant systems, such as DNA/RNA nucleobases, protein chromophores and phototherapeutic compounds in different environments: gas-phase, solvated and biological media. Such studies are complemented by computing reaction dynamics in the excited states using direct ab initio semiclassical trajectory techniques.

Special Techniques: Ab initio multiconfigurational quantum chemistry: CASSCF and CASPT2 methods. Determination of minimum energy reaction paths, conical intersections and intersystem crossings. Chemical environment simulations: continuum and QM/MM techniques. Direct ab initio reaction dynamics with semiclassical trajectories. Methods and programs development: the quantum-chemistry MOLCAS code.

1. L. Serrano-Andrés and M. Merchán. *J. Photochem. Photobiol. C: Photochem. Rev.* **2009**, *10*, 21.

2. G. Olaso-González, M. Merchán, and L. Serrano-Andrés: *J. Am. Chem. Soc.*, **2009**, *131*, 4368.
3. L. Serrano-Andrés, M. Merchán, A. C. Borin, *J. Am. Chem. Soc.* **2008**, *130*, 2473.
4. D. Roca-Sanjuán, G. Olaso-González, I. González-Ramírez, L. Serrano-Andrés, and M. Merchán. *J. Am. Chem. Soc.*, **2008**, *130*, 10768.
5. L. Serrano-Andrés, M. Merchán, and A. C. Borin. *Proc. Natl. Acad. Sci. USA*, **2006**, *103*, 8691.

Centre: Molecular Science Institute. Group of Photochemical Reactivity

Research Group: Prof. Dr. Julia Pérez-Prieto (Head of the Group); Dr. Elena Zaballos, Dr. Raquel Eugenia Galian, Dr. Luciana Carina Schmidt; Salvador Pocoví-Martínez, Jordi Aguilera Sigalat, Miriam Parreño, Jaime; Carlos Agudelo.

Research Interests: Design and synthesis of new photosensitisers. Study of inter- and intramolecular reactions between chromophores at the ground state and the excited state, as a way to obtain, by selective excitation, selective photocatalysts for organic synthesis. Design, synthesis, and application of functional hyperbranched polymers as photocatalysts, chiral sensors, antioxidants, and ultraviolet photoprotectors. Design and synthesis of functional semiconductor and metallic nanoparticles.

Special Techniques: Steady-state and time-resolved fluorescence. Nanosecond laser flash photolysis.

1. A. El Moncef, M. C. Cuquerella, E. Zaballos, C. Ramírez de Arellano, A. Ben-Tama, S-E. Stiriba, J. Pérez-Prieto *Chem. Commun.* **2010**, *46*, 800.
2. M. C. Cuquerella, S. Pocoví-Martínez, J. Pérez-Prieto, *Langmuir*, **2010**, *26*, 1548.
3. R. E. Galian, M. De la Guardia, J. Pérez-Prieto, *J. Am. Chem. Soc.* **2009**, *131*, 892.
4. L. Pástor-Pérez, E. Barriau, H. Frey, J. Pérez-Prieto, S.E. Stiriba, *J. Org. Chem.*, **2008**, *73*, 4680.
5. J. Pérez-Prieto, R. E. Galian, M. C. Moránt-Miñana, *ChemPhysChem*, **2006**, *7*, 2077.

University of the Basque Country
Centre: Faculty of Science and Technology

Research Group: Iñigo López Arbeloa; Fernando López Arbeloa, Virginia Martínez Martínez; Jorge Bañuelos Prieto; Teresa Arbeloa López; Cecilia Corcóstegui Ruiz-Carrillo; Leire Gartzia Rivero

Research Interests: Photophysical study of organic probes in nanostructured and mesoporous materials (one, two, three-dimensions). These research lines are aimed towards advanced applications of photoactive functional and multifunctional materials of interest in photonics, renewable energies, catalysis, etc... Molecular engineering of pyromethenes and other laser dyes aiming at the development of synthonisable lasers in the solid media in the red and blue regions. The incorporation of dyes in different nanostructured materials of one, two, and three dimensions, allows the preparation of highly ordered photoactive systems of application in non-linear optics, as generators of the second harmonic, light emitting diodes (LEDs), luminiscent concentrators, sensors, etc. Another aim of the group is the design of antenna systems with a hybrid supramolecular organisation to improve the efficiency of organic solar cells. Finally, the group is concentrating on the application of confocal fluorescent microscopy in the study of structures generated by organic ligand assembly with metallic ions (metal-organic framework, MOFs), which have important technological perspectives.

Special Techniques: steady-state and time-resolved (ps) fluorescence spectroscopy. Scanning confocal fluorescence microscopy for single-molecule analysis (temporal and spectral resolution)

1. S. Salleres, F. López Arbeloa, V. Martínez, T. Arbeloa and I. López Arbeloa, *Langmuir*, **2010**, *26*, 926.
2. A. Costela, I. García-Moreno, M. Pintado Sierra, F. Amat-Guerri, R. Sastre, M. Liras, F. López Arbeloa, J. Bañuelos and I. López Arbeloa, *J. Phys. Chem. A*, **2009**, *113*, 8118.
3. S. Salleres, F. López Arbeloa, V. Martínez, T. Arbeloa and I. López Arbeloa, *J. Phys. Chem. C*, **2009**, *113*, 965.
4. J. Bañuelos, F. López Arbeloa, T. Arbeloa, S. Salleres, F. Amat-Guerri, M. Liras and I. López Arbeloa, *J. Phys. Chem. A*, **2008**, *112*, 10816.
5. I. Garcia-Moreno, F. Amat-Guerri, M. Liras, A. Costela, L. Infante, R. Sastre, F. López Arbeloa, J. Bañuelos Prieto, I. López Arbeloa, *Adv. Funct. Mat.* **2007**, *17*, 3088.

ACTIVITIES OF RESEARCH CENTRES

Centre for Oxygen Microscopy and Imaging, Aarhus, Denmark

Singlet Oxygen Microscopy and Imaging

The Center for Oxygen Microscopy and Imaging (COMI) at Aarhus University is a multifaceted research center focusing on the many roles that singlet molecular oxygen, $O_2(a^1\Delta_g)$, plays in modern chemistry, physics, biology and medicine. This article intends to provide a brief historic presentation of COMI, an overview of selected ongoing scientific activities and an outlook to what the immediate future may hold for singlet oxygen-based spectroscopy and imaging, particularly in studies performed at the level of single biological cells.

Who are We and What Do We Do

In 2002 the Center for Oxygen Microscopy was established with funding from the Danish Research Council. The scientific program was focused on studying singlet oxygen photophysics in a variety of systems, ranging from liquids to heterogeneous polymers and biological cells. These research activities were expanded significantly in 2005, as financial support from the Danish National Research Foundation to cover a 5 year period (2005-2010) allowed for the founding of The Center for Oxygen Microscopy and Imaging (COMI).

COMI is an interdisciplinary center headed by professor Peter R. Ogilby at the department of chemistry at Aarhus University. Capitalizing on the scientific achievements and developments started back in 2002, the birth of COMI marked the beginning of more expansive and diverse scientific endeavours. Combining "classic" singlet oxygen photophysics and spectroscopy with additional expertise in such different fields as computational chemistry, electrochemistry and electrophysiology, COMI set out to establish a

broad platform for studying singlet oxygen in complex systems of general scientific importance.

Specifically, the development of tools to study the pertinent processes occurring at the level of single cells has been a cornerstone in the work performed over the past 5 years. Indeed, the most prominent scientific results to emerge from COMI have arguably come from what we have coined “the singlet oxygen microscope”. Here microscopy and imaging techniques are combined with laser-based singlet oxygen spectroscopy to reveal mechanistic information from small spatial domains in heterogeneous systems, including single biological cells.

Additional and complementary work has focused on electrochemical and electrophysiological studies, whereas a long-term project is concerned with the theoretical description of aspects of the unique and challenging oxygen-organic molecule photosystem. Another important part of the work in COMI is the optimization of suitable organic molecules to be used as photosensitizers and drugs, as well as the development of novel nano-metallic particles to enhance weak optical signals. All of this involves organic synthesis and chemical and physical engineering of nano-metallic structures.

On average the core activities in COMI employ approximately 15-20 people who include senior scientists, postdoctoral fellows and PhD students from Denmark and abroad. Additionally, we are fortunate to have many fruitful collaborations with scientists around the world. The broad scope of our program is reflected in the instrumentation we employ, which spans the toolbox of the modern spectroscopist (femtosecond lasers, modified commercial microscopes, sensitive near-IR detectors etc.) to that of the molecular biologist (cell-handling techniques, genetic engineering etc).

Following renewed support from the Danish National Research Foundation, COMI is currently entering a new 5 year grant period (2010-2015), wherein we will be looking to continuing and increasing our efforts to gain insight into the fascinating chemistry, physics and biology of singlet oxygen.

Scientific Scope and Selected Results

In 2010, one no longer needs to justify why research on singlet oxygen is important. The ubiquitous nature of oxygen, light and organic molecules has long caused the scientific community to recognize that singlet oxygen is a unique reactive species that influences systems throughout chemistry, physics, biology and

medicine. Still, problems involving singlet oxygen continue to challenge our scientific understanding and show non-trivial behaviour in different and complex systems. Of particular interest is the attention given to singlet oxygen as a key reactive intermediate in Photodynamic therapy (PDT), wherein cancerous tissue can be destroyed following photosensitized production of singlet oxygen. As such, a large fraction of the forefront of singlet oxygen research is concerned with optimizing and developing drugs and understanding the complicated mechanisms of cell death initiated by singlet oxygen. Producing and detecting singlet oxygen remains a central theme of our activities in COMI, and the Jablonski diagram in Figure 1 encompass essential elements of our research.^[1] Briefly, a photosensitizer molecule is excited following either one- or two-photon excitation, to eventually produce the lowest excited singlet state. In competition with radiative and non-radiative deactivation to the ground state, the sensitizer can relax to produce a comparatively long-lived triplet state which can be quenched by ground state oxygen, $O_2(X^3\Sigma_g^-)$, to generate singlet oxygen, $O_2(a^1\Delta_g)$, via an energy transfer mechanism. Subsequently singlet oxygen can be monitored by its characteristic near-IR phosphorescence at ~ 1275 nm.

At this juncture it is important to recognize that the vast majority of singlet oxygen molecules do not decay by this emissive pathway as the emission quantum yield is typically 10^{-5} - 10^{-7} . This fact often makes the direct optical detection of singlet oxygen phosphorescence an experimental challenge in its own. Rather, singlet oxygen molecules are predominantly removed via collisions with the solvent or reactions with various molecules in the system. In this regard, singlet oxygen is both a highly reactive as well as highly selective oxygen species that has affinity for a wide range of organic and bioorganic molecules.

In the conceptually simple approach in Figure 1 lies several subtleties and fundamental scientific challenges, in particular with respect to experiments performed in biological cells. First of all, there is the choice of the sensitizer. This is “the drug” used in PDT, for example, which obviously puts restrictions on suitable molecules, as issues of cellular uptake and localization as well as non-toxicity and biocompatibility must be considered. Clearly the sensitizer must produce singlet oxygen in high yield, i.e. have a large singlet oxygen

quantum yield, Φ_{Δ} , but appreciable fluorescence is also desirable in cases where the sensitizer emission is used as the optical probe.

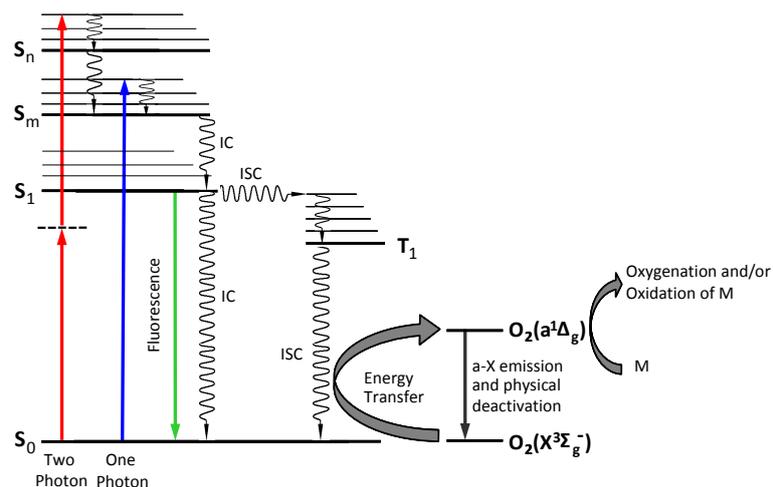


Figure 1 Diagram illustrating the one- and two-photon-initiated, triplet-state photosensitized production of singlet oxygen. The letters S and T denote discrete states of the sensitizer with singlet and triplet spin multiplicity, respectively. IC and ISC denote internal conversion and intersystem crossing, respectively. M denotes an organic molecule.

Two-Photon Photosensitized Production of Singlet Oxygen

It is often the case that the sensitizer in question efficiently absorbs light in a one-photon process, i.e. that it possesses a large one-photon absorption cross section. However, much recent effort has been spent on optimizing molecules that are characterized by comparatively large two-photon absorption (TPA) cross sections, δ .

A main rationale for optimizing this latter nonlinear property is to take advantage of the fact that a focused laser beam will only allow TPA to occur in a small focal volume (as opposed to linear one-photon absorption which will occur throughout the light path), thereby giving high three-dimensional resolution, Figure 2. Another advantage for biological purposes comes from the experimental fact that a typical TPA process is driven by excitation light in the near-IR

region of the spectrum, where scattering of the laser light is minimized and penetration into the sample is maximized.

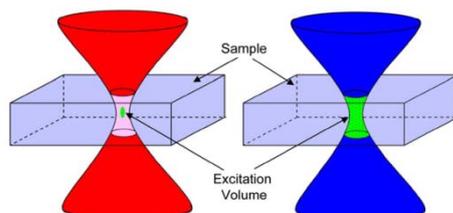


Figure 2 Different excitation volumes (shown in green) upon two-photon(left) and one-photon (right) excitation by a focused laser.

Over the past decade, the scientific community has been examining various classes of organic molecules with respect to their non-linear optical behaviour. Figure 3 shows examples of some of the molecules we have been investigating in COMI. By and large, there is demand for organic molecules which will efficiently produce singlet oxygen and possess large TPA cross sections. That is to say, one must try to optimize the overall product $\delta \Phi_{\Delta}$. However, this issue is complicated by the fact that optimizing, for instance, the charge-transfer character of a molecule is conducive for large values of δ , but will generally result in small values of Φ_{Δ} . Hence, much of the current defining research is devoted to understanding and optimizing factors that contribute to δ and Φ_{Δ} , and this involves insight into chemical design strategies and the basic photophysics.

To this end, our contributions have included combined experimental and computational studies of, for example, effects of molecular symmetry and solvent.^{[2],[3]} Experimental techniques to accurately measure TPA spectra and cross sections have progressed to the point where such experiments are now implemented on a “routine” basis. However, the computational community must still overcome significant challenges before one can compare quantitatively rather than qualitatively with experiments. In addition to developing more efficient and computationally tractable theoretical methods, such as response theory, one must specifically consider vibrational degrees of freedom as well as solvent-solute interactions. Current work attempts to use hybrid quantum mechanics/molecular mechanics models to address these complicated issues.^[4]

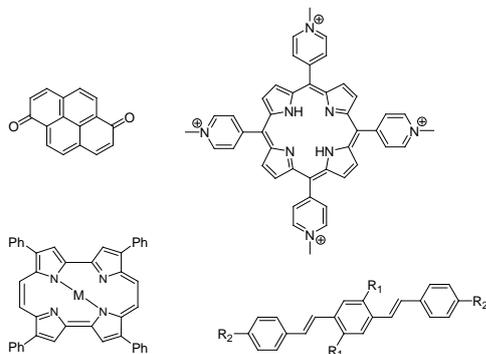


Figure 3 Examples of molecules and classes of molecules that have been studied as two-photon singlet oxygen sensitizers.

Monitoring Singlet Oxygen in Cells

The direct time-resolved spectroscopic detection of the near-IR singlet oxygen phosphorescence remains a unique optical probe when performing experiments on biological cells.^[5] Crucial experimental information comes from the temporal concentration profile of singlet oxygen, eq. 1, and the observed singlet oxygen lifetime, τ_{Δ} , given by eq. 2.

$$[{}^1\text{O}_2(t)] \propto \{\exp(-t / \tau_T) - \exp(-t / \tau_{\Delta})\} \quad (1)$$

$$\tau_{\Delta}^{-1} = (k_{nr} + k_r)[S] + \sum_j k_j [j] \quad (2)$$

Eq. 1 reflects the scheme in Figure 1 for the triplet state photosensitized production of singlet oxygen. Here τ_T is the lifetime of the singlet oxygen precursor; the sensitizer triplet state. In eq.2, k_{nr} and k_r are the rate constants for non-radiative and radiative deactivation of singlet oxygen by the solvent S, which, in most cases results in a lifetime in the microsecond domain. However, as discussed, singlet oxygen is readily removed by other species, j, in the system each characterized by an overall rate constants k_j . This includes the reactions that make singlet oxygen pertinent for PDT. In this way, the temporal kinetic profile showing singlet oxygen

formation and decay reflect the chemical and physical composition of the system.

One illustration of this is shown in Figure 4, where singlet oxygen is detected from a single D₂O-incubated cell following excitation of an intracellular photosensitizer.^[6] With prolonged irradiation, we observe a decrease in the rate at which singlet oxygen is formed and a decrease in the rate at which singlet oxygen is removed (i.e. τ_A increases).

It has been demonstrated that the behavior in Figure 4 is an immediate consequence of an increase in the local intracellular viscosity following the PDT treatment. Because both formation and quenching of singlet oxygen are bimolecular diffusion-mediated processes, this increase in viscosity is directly manifested in the respective kinetics.

A key aspect of the data presented in Figure 4 is that it was obtained using focused laser excitation to provide subcellular resolution. In related work we have shown that the kinetic behavior of singlet oxygen in a cell is spatially dependent.^[7] To be able to irradiate with high selectivity and control is a vital premise as a cell is inherently heterogeneous with both polar and non-polar domains where sensitizer localization and oxygen diffusion, solubility and reactivity will invariably differ.

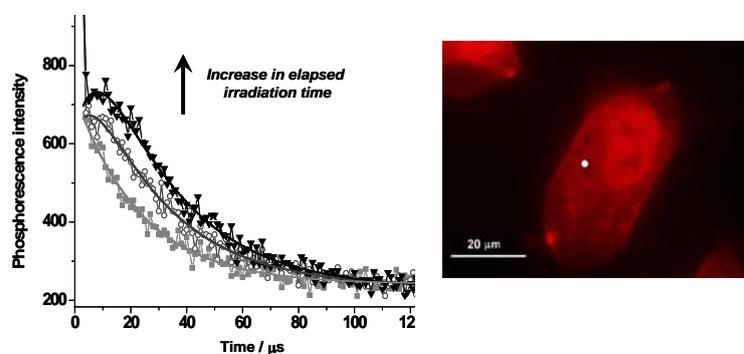


Figure 4 *Left:* time-resolved singlet oxygen phosphorescence signals recorded from a single D₂O-incubated HeLa cell as a function of the elapsed irradiation time of the sensitizer. *Right:* image of another HeLa cell created using sensitizer fluorescence. The white spot located in the cytoplasm represents the approximate cross-sectional size of the focused laser beam.

Figure 5 shows some of the quite dramatic morphological changes that can occur when cells are subjected to singlet-oxygen induced PDT.^[8] Here, HeLa cells containing Yellow Fluorescent Protein (YFP) genetically encoded in the tubulin cytoskeletal network, were incubated with a singlet oxygen sensitizer and then subjected to non-focused irradiation. As the YFP-based images clearly demonstrate, the cytoskeletal network collapses upon perturbing the cell by irradiating the sensitizer. We have independently demonstrated that similar changes can even be induced by localized excitation, a reminder that although singlet oxygen may be formed locally it may affect the overall viability of the whole cell.

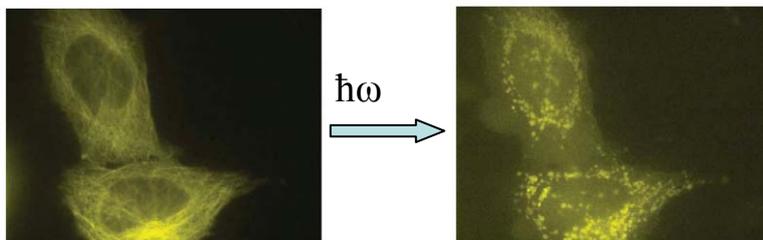


Figure 5 *Left:* image of two HeLa cells based on emission from YFP in the tubulin cytoskeletal network. *Right:* YFP-based image that shows the collapse of the cytoskeletal network upon one-photon irradiation of an intracellular sensitizer.

Enhanced Emission Using Metal Nanoparticles

Despite many successful experiments relying on singlet oxygen emission as the optical probe, one is often still severely limited by the very low phosphorescence yield and the fact that the signal is in the near-IR where detector sensitivity is much less than in the UV-Vis region. As such, there is much to gain if one could potentially boost the singlet oxygen phosphorescence intensity. One approach, which we explore in COMI, is to overcome this obstacle by using metal nanoparticles in both solid and liquid phase systems to enhance the emission.

In one series of studies, we used lithographic techniques to design gold nano-discs that allow accurate tuning of the pertinent optical properties of the metal particle.^[9] Specifically, by changing the diameter to height aspect ratio one can tune the disc plasmon

resonance to be either on- or off-resonant with the spectral profile of singlet oxygen emission at ~ 1275 nm. This is shown in Figure 6, where a change in disc diameter from 150 nm to 260 nm effectively moves the plasmon resonance from 830 to 1250 nm. Upon generating singlet oxygen following excitation of a sensitizer, we have demonstrated that when comparing the on-resonance sample with a control sample, we can indeed increase in the singlet oxygen signal. Even the off-resonance sample gives a small enhancement as this sample also has a non-zero extinction at 1275 nm. Boosting the singlet oxygen signal this way may help open up for even more sensitive experiments performed at the single-cell level.

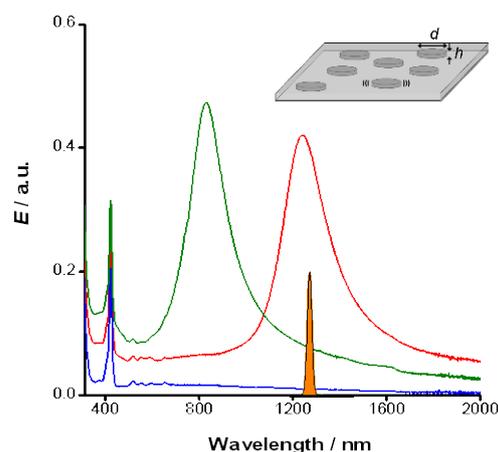


Figure 6 Pertinent extinction spectra in sensitizer-containing polystyrene matrices: — no discs, — off-resonance discs, — on-resonance discs. The spectral emission profile of singlet oxygen is indicated by the curve filled with orange.

However there is ample room for improvement, and the proof-of-principle experiment in Figure 6 is just the beginning. In fact, a simple calculation shows that only about 1 % of the singlet oxygen molecules are close enough to be influenced by the unique electric field associated with the gold-nano discs. As such, a conservative estimate puts the true enhancement factor orders of magnitude higher.

To address this issue, and to construct more mobile systems suitable for biological applications, we are currently working on producing multilaminate nano-particles for enhancement in the aqueous phase. An example of such structures is shown in Figure 7.^[10] Here gold nanorods are coated with a silica shell onto which a gold overcoat is grown. This produces an interaction between the inner gold rod and the outer gold layer, which results in unique optical properties. Furthermore, these properties can be predictably tuned by varying the parameters of the system, i.e. the dimensions of the nano-rod and the thicknesses of the silica shell and gold overcoat.

Still, there are several complicating factors when dealing with such solution phase chemistry, and an integral part of the work yet to be done involves proper functionalization of the metallic nano-particles such that a desired chromophore can be directly attached to the particle. By controlling the density of chromophores and their distance to the particle we hope to create a robust system where the enhancement can be maximized.

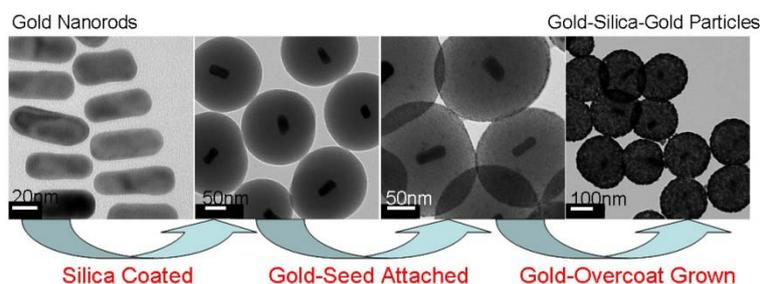


Figure 7 Left-to-right: Bare gold nanorods are first coated with a silica shell onto which a gold overcoat is then grown to yield multilaminate gold-silica-gold structures.

Future perspectives

There can be no doubt that the study of singlet oxygen remains ever topical and of global scope. The community is increasingly probing more sophisticated systems and uncovering new mechanistic information about what is really happening in complex biological media. But at the same time new questions arise and the number of variables in the investigated systems grows. As experimentalists we must continue to develop new techniques to monitor and control the multitude of processes that occur. Also, and as a joined effort, we

must continue to hold hands with the computational chemists as they can offer an independent and complementary perspective.

In COMI we are currently working on a number of projects aimed at addressing these issues. Imaging based on singlet oxygen phosphorescence and/or sensitizer fluorescence are indeed powerful tools, yet additional information can be obtained by combining these optical methods with highly sensitive electrophysiological measurements. With the latter approach one can monitor the concentration of intracellular ions (e.g. Ca^{2+}) and various membrane potentials. In this way electrophysiological techniques can be used, in conjunction with well-established optical assays, as an instrument to assess cell viability following the generation of singlet oxygen.

Some of our projects also attempt to capitalize on so-called tagging techniques from molecular biology, wherein one can covalently link a given chromophore onto a specific intracellular protein. In this way one can attach molecules that either produce singlet oxygen, quench singlet oxygen or act as fluorescence-based traps for singlet oxygen. Through these studies it will be possible to achieve even higher degree of specificity when localizing a given PDT drug. Also, by judiciously incorporating molecules that respond to the presence of singlet oxygen (i.e. quenchers or traps) one can imagine designing elaborate experiments to very accurately quantify singlet oxygen diffusion and activity with very high spatial resolution.

To learn more about the people and science in COMI, visit our website at:

<http://www.chem.au.dk/~comi/>

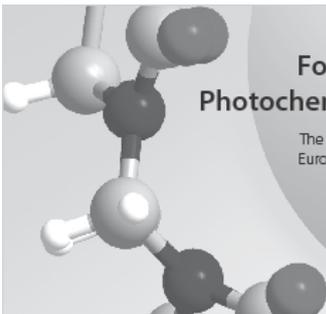
Representative recent publications from COMI

- [1] Singlet Oxygen: There is Indeed Something New Under the Sun, *Chem. Soc. Rev.* **2010**, DOI:10.1039/B926014P.
- [2] Two-Photon Absorption in Tetraphenylporphycenes: Are porphycenes better candidates than porphyrins for providing optimal optical properties for two-photon photodynamic therapy?, *J. Am. Chem. Soc.*, **2007**, *129*, 5188-5199.
- [3] Effect of Solvent on Two-Photon Absorption by Vinyl Benzene Derivatives, *J. Phys. Chem. A*, **2008**, *112*, 7831-7839.
- [4] Overview of Theoretical and Computational Methods Applied to the

- Oxygen-Organic Molecule Photosystem, *Photochem. Photobiol.*, **2006**, 1136-1160.
- [5] Optical detection of singlet oxygen from single cells, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 4280 - 4293.
- [6] Imaging Intracellular Viscosity of a Single Cell during Photoinduced Cell Death, *Nature Chemistry*, **2009**, *1*, 69-73.
- [7] Singlet Oxygen in a Cell: Spatially Dependent Lifetimes and Quenching Rate Constants, *J. Am. Chem. Soc.*, **2009**, *131*, 332-340.
- [8] Photosensitized Production of Singlet Oxygen: Spatially-Resolved Optical Studies in Single Cells, *Photochem. Photobiol. Sci.*, **2009**, *8*, 442-452.
- [9] Enhanced 1270 nm Singlet Oxygen Phosphorescence, *Ang. Chem. Int. Ed.*, **2008**, *47*, 6025-6027.
- [10] Silica-Coated Gold Nanorods with a Gold Overcoat: Controlling Optical Properties by Controlling the Dimensions of a Gold-Silica-Gold Layered Nanoparticle, *Langmuir*, **2010**, *26*, 4188-4195.

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 PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



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- Mimicking the antenna system of green plants by G Calzaferri and K Lutkouskaya
- Time-resolved fluorescence microscopy by K Suhling, PNW French and D Phillips
- Effects of solar UV radiation on aquatic ecosystems and interactions with climate change by DP Hader, HD Kumar, RC Smith et al.
- Milestones in the development of photodynamic therapy and fluorescence diagnosis by A Juzeniene, Q Peng and J Moan
- Combining intracellular and secreted bioluminescent reporter proteins for multicolor cell-based assays by E Michelini, L Cevenini, L Mezzanotte et al.

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Organic Chemistry Department, University of Pavia

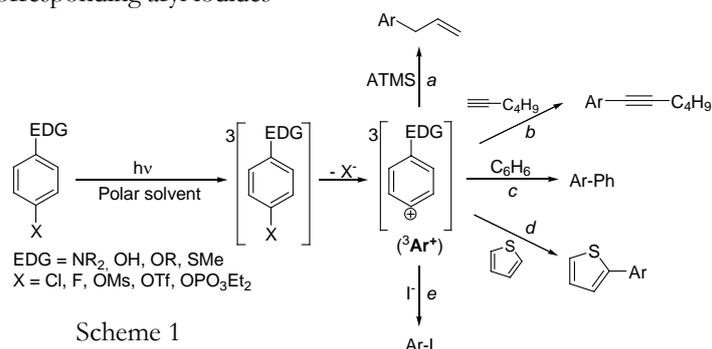
Supervisor: Prof. Albini

The formation of aryl-carbon bonds is one of the most important, as well as difficult, targets of organic synthesis. Modern arylation methods are based on organometallic chemistry; the photochemical approach, however, offers an alternative that is in accord with the green chemistry principles (actually light is *the* clean reagent) and has a large synthetic potential not fully exploited as yet. This method is based on the electronic excitation of the starting compounds that leads to the generation of high-energy intermediates (such as aryl radicals Ar \cdot or cations Ar $^+$), under mild conditions.

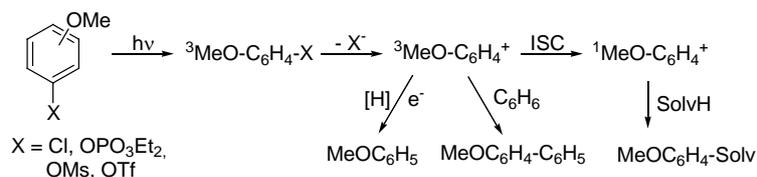
The heterolytic fragmentation of substituted aromatics to give a phenyl cation has been initially deemed as a rare occurrence, because of the high instability of the latter species, but recently our research group has demonstrated that heterolytic cleavage is the main photochemical process from the triplet excited state of phenyl fluorides, chlorides, mesylates, triflates and phosphates bearing an amino, alkoxy, hydroxy or alkylthio group in the *para* position (Scheme 1).

Irradiation of these substrates in polar media (e.g. water/acetonitrile mixtures, methanol or 2,2,2-trifluoroethanol) leads to the corresponding *triplet* aryl cations ($^3\text{Ar}^+$), which exhibit a high reactivity towards π nucleophiles, such as alkenes, alkynes and arenes (differently from the unselective singlet). With allyltrimethylsilane (ATMS), for example, the leaving group Me $_3\text{Si}^+$ is lost from the adduct cation and an allylbenzene is efficiently formed (Scheme 1, path *a*). Arylation of alkynes is likewise successful and offers an alternative to the Sonogashira reaction for the preparation of

arylalkynes (path *b*), while the generation of phenyl cations in the presence of benzene leads to biphenyls (path *c*). Even more interesting is the selective arylation in position 2 of five-membered heterocycles, such as pyrrole and thiophene (path *d*). Phenyl cations can also react with inorganic anions (e.g. iodide, path *e*), giving the corresponding aryl iodides



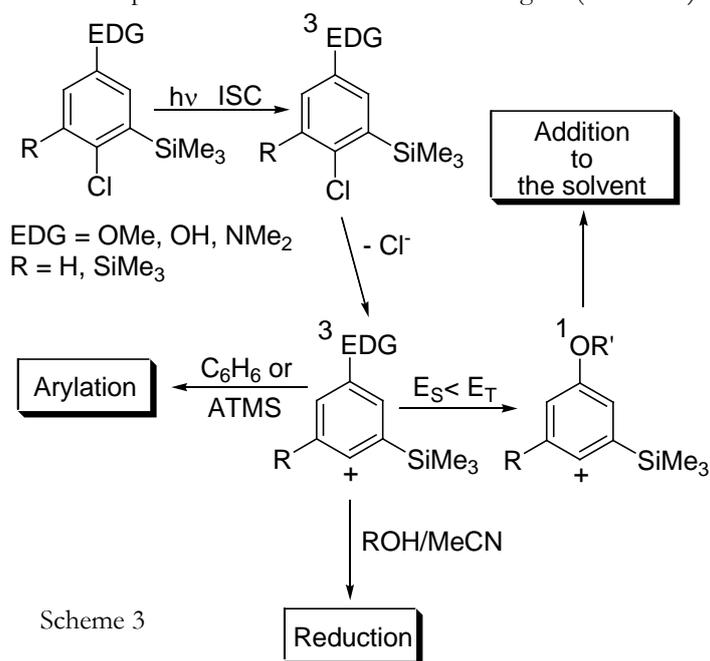
Overall, the reaction can be viewed as a photo-S_N1 reaction of the aromatic derivative and the main purpose of the present thesis has been both to explore further synthetic applications of such process and to better understand the chemistry of aryl cations from a mechanistic point of view. First, I have considered the effect of the position of the substituent by investigating the photoreactivity of the three isomeric chloroanisoles and of the corresponding methoxyphenyl esters (mesylates, triflates and phosphates), in solvents having different polarity, both neat and in the presence of benzene, as a typical π trap for electrophiles (Scheme 2).



The triplet methoxyphenyl cations formed by photolysis react with π nucleophiles or, in neat solvent, are reduced to anisole. On the

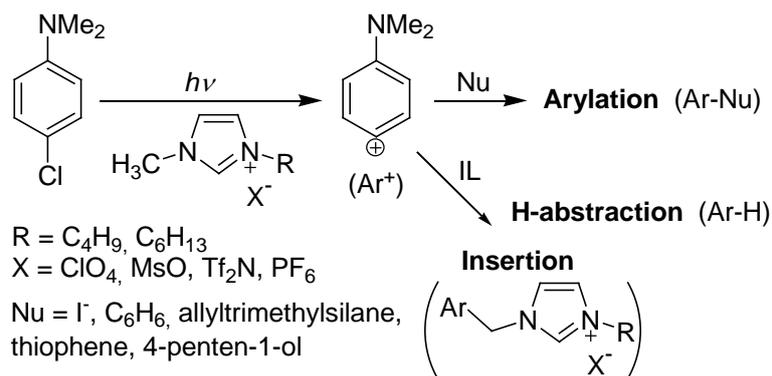
contrary, solvolysis is attributed to the singlet cations (that, as mentioned above, is an unselective electrophile), formed by intersystem crossing (ISC) from the corresponding triplet. The substituent orientation does not influence the efficiency of the photocleavage, but has a marked effect on the key intermediate, the phenyl cation: the *meta* substituted singlet is selectively stabilized, and ISC from the initially formed triplet is favored. This peculiar stabilization is a new, though conceptually different, interesting example of the so called “*meta* effect” in photochemistry.

Another aspect that has been evaluated is the influence of additional substituents in the aromatic ring on the photochemistry of electron-rich aryl halides. In particular, silicon based substituents, such as the trimethylsilyl (TMS) group, are well known to stabilize a positive charge present on a beta position and to facilitate the thermal generation of phenyl cations in solution. In order to assess the β -effect of silicon on the photochemical generation of such intermediates, the photoreactivity of some aryl chlorides bearing one or two TMS substituent(s) in *ortho* with respect to the leaving group has been compared with that of silicon-free analogues (Scheme 3).



Both calculations and steady-state experiments clearly show that the presence of a trimethylsilyl group in *ortho* to the leaving chlorine strongly stabilizes the singlet cation to the extent that it becomes the *reactive* spin state. As a result the chemistry expected from the triplet (reduction or C-arylation) is replaced by that of the singlet (solvolysis, and thus O or N arylation).

As for the reaction medium, a class of novel and environmental benign solvents, the polarity of which is similar to that of acetonitrile or alcohols, is represented by room temperature ionic liquids (ILs). In order to evaluate the role of the solvent in the reactivity of phenyl cations, the photoreactivity of 4-chloro-*N,N*-dimethylaniline (previously studied in organic solvents of different polarity), has been explored in five *N*-methyl-*N*-alkylimidazolium salts, in the presence of several nucleophiles (Scheme 4).

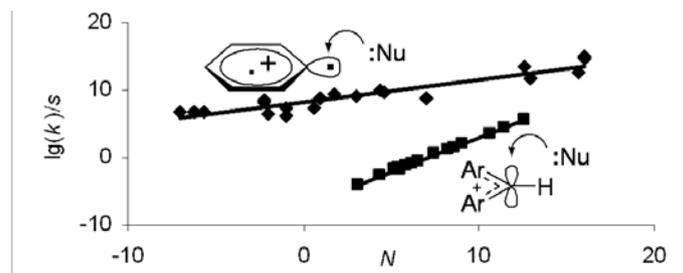


Scheme 4

The high viscosity of such media and their specific interactions with 4-*N,N*-dimethylaminophenyl cation markedly affect the products distribution, as compared to that obtained in a solvent like acetonitrile. In fact, in the absence of nucleophiles, the triplet 4-Me₂N-C₆H₄⁺ can abstract a hydrogen from the alkyl chains of imidazolium ring, to afford *N,N*-dimethylaniline (Ar-H, Scheme 4), but can also give insertion into a C-H bond of the imidazolium methyl group. The presence of π traps (e.g. alkenes or arenes) and inorganic anions (such as iodide), however, allows the formation of the corresponding arylation products (Ar-Nu), in yields similar or even higher than those obtained in acetonitrile. As for the above, it

emerges that ILs are inert towards highly reactive species such as phenyl cations, provided that the concentration of the nucleophile is high enough to avoid undesired side-reactions. Thus ILs can be convenient media for carrying out syntheses involving highly reactive intermediates.

The last issue considered during the mechanistic study is the selectivity of aryl cations towards different classes of nucleophiles (σ , π e n). Singlet 4-Me₂N-C₆H₄⁺ reacts at diffusion controlled rate with any kind of nucleophiles. The triplet cation, however, shows a certain degree of selectivity and allows to build a nucleophile-electrophile reactivity scale in analogy to that previously reported based on benzhydrylium ions (Scheme 5).



Scheme 5

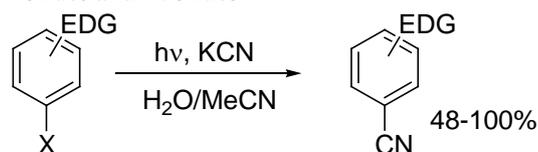
A synthetic application that has been found viable is trapping with benzenes. This is useful because biaryls actually represent common substructures in many pharmaceutically and biologically active molecules; their synthesis can be accomplished by the reaction of phenyl cations with arenes. Irradiation of several substrates in trifluoroethanol, in the presence of symmetrical methylbenzenes (*p*-xylene, mesitylene and durene), allowed to prepare a series of biaryl compounds, including sterically congested examples, in high yields (52-84%, Scheme 6).



Scheme 6

Photochemical S_N1 arylation reactions were again strictly chemoselective: neither functionalization at benzylic positions nor multiple arylation were observed and other possible competitive pathways, such as the reduction of the starting halides or sulfonate/phosphate esters, were always negligible. In fact, this novel photochemical synthesis of biaryl compounds represents a convenient and 'green' alternative to organometallic mediated processes.

Further synthetic applications are based on the fact that, as mentioned above, triplet aryl cations smoothly react with charged nucleophiles. Thus, the photoreactivity of several electron-rich aryl halides and esters in the presence of cyanide ion has been explored (Scheme 7), to synthesize different benzonitriles which find large applications as agrochemicals and pharmaceuticals. A mild photoinduced cyanation protocol was finally achieved at room temperature, by using a cheap cyanating agent (KCN) and aqueous acetonitrile as the solvent and benzonitriles are formed in good to excellent yields. In contrast to palladium catalyzed processes, the present photochemical method requires extremely mild conditions and applies to precursors less reactive under thermal conditions, such as phenyl chlorides and fluorides.



Scheme 7

Carlo Giansante

Supramolecular Photoactive Systems

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Supervisor: Prof. Vincenzo Balzani

Chemists deal with matter and its transformations. They create molecules rearranging atoms –but handling molecules– into an infinite variety of combinations, at least until they have imagination. Some of them hold molecules together trying to gain control on increasing matter complexity.

Complexity does not result by mere addition of molecular components, but implies their mutual interactions. Novel features appear at each level of complexity, peculiar of the whole system rather than of the sum of its components. Such features characterize each level of complexity and cannot exist, even conceptually, at the levels below. It's however on the basis of the chemical components at lower levels, their mutual interactions and integrating them in order to connect a level to the others that increasing complexity can be described and explained. Supermolecules are organized entities resulting from the self-assembly of two or more chemical species held together by intermolecular forces.¹ Supermolecules thus represent a further step towards complexity compared to molecules as the latter do to atoms.

Nuclei and electrons are charged particles and their motions in atoms and molecules generate oscillating electric and magnetic fields. Light consists of oscillating electric and magnetic fields. Whether the frequencies of such oscillations in light and chemical species match, matter can absorb energy from light. Light absorption is indeed widely used to investigate matter. In this regard, photochemistry describes chemico-physical processes occurring in molecules that undergo electronic transitions upon absorption of near ultraviolet and visible light.

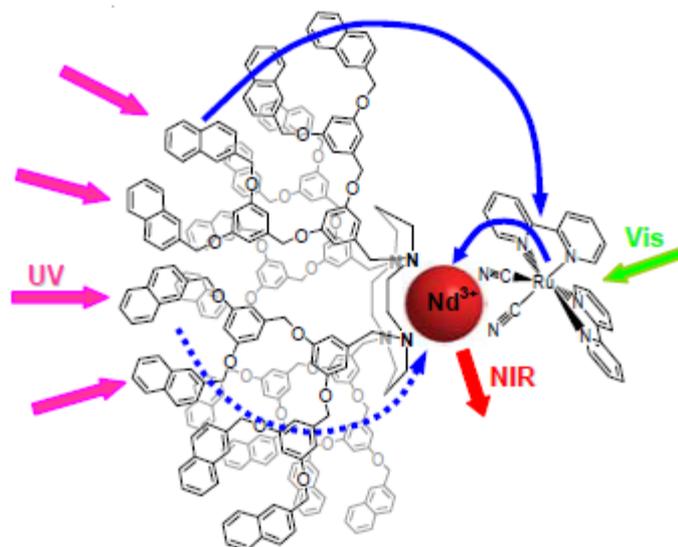
As a result, supramolecular photochemistry deals with entities constituted by self-assembled photoactive components that may undergo mutual perturbation upon light absorption. Novel photophysical and photochemical properties peculiar of the supramolecular systems thus arise and such properties do not result

from the simple superposition of those of the component units. Photoinduced processes involving two or more self-assembled components, such as energy, electron or proton transfer, substrate binding, photochemical reactions, catalysis, etc. take place in a supermolecule rather than between its constituting isolated units.

Self-assembly of molecular components by weak, non covalent interactions is a widespread concept to Nature's forms and functions² and is attracting increasing interest in artificial systems conceived to control mechanical movements, process information, and harvest sunlight.³ In this regard, the present PhD thesis has been dedicated to the study of some supramolecular photoactive systems that act as antennas capable of collecting incident light and exploiting it to transfer electronic energy or electrons from one molecular component to another. The molecular components of the supramolecular systems investigated in this thesis are dendrimers, molecular tweezers, macrocycles and metal complexes that have been synthesised elsewhere (Bonn, Los Angeles, Essen, Zurich, Strasbourg, Moscow).

A noteworthy example is represented by the self-assembly of a threecomponent light-harvesting antenna comprising a dendrimer, a ruthenium complex and a neodymium ion (see figure). New features arise from their self-assembly. The dendrimer has a very high molar absorption coefficient in the near UV spectral region due to 12 dimethoxybenzene and 16 naphthyl chromophoric units constituting its framework; it is luminescent and presents a single coordinating site located in the core, which can strongly bind trivalent lanthanide ions, but it is unable to sensitize their luminescence. The $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$ complex shows absorption and emission properties highly sensitive to the presence of cations and can coordinate Nd^{3+} ions by the cyanide ligands and sensitize its emission. Mixing such three species in 1:1:1 molar ratio an unusual Nd^{3+} complex, exploiting the dendrimer and the Ru^{2+} complex as ligands, self-assembles in solution. The resulting supramolecular system behaves as a molecular-level antenna that harvests ultraviolet and visible light and exhibits luminescence in the near infrared region. The sensitization of the Nd^{3+} ion luminescence has been achieved upon excitation of the naphthyl chromophores of the dendrimer through the Ru^{2+} complex that behaves as a luminescent mediator (full blue lines in figure), while in the absence of the Ru^{2+} complex component the dendrimer is unable to transfer the excitation energy to the Nd^{3+}

ion, even though it is directly coordinated to it (dotted blue line in figure).⁴



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Thomas Härtling

Photochemical Tuning of Surface Plasmon Resonances in Metal Nanoparticles

Technische Universität Dresden
Supervisor: Prof. Lukas Eng

Illuminated metal nanoparticles (MNPs) feature collective electron oscillations (so-called localized surface plasmons or LSPs) which facilitate concentrating light-matter interactions to length scales below the diffraction limit. Part I of this book describes two applications of this confinement effect. Firstly, the use of single particles as optically active probes for scanning near-field optical microscopy is demonstrated. Secondly, fluorescence enhancement in the vicinity of a single MNP is described theoretically. This description focuses on how the particle diameter and the surrounding medium influence the enhancement. It turned out that in these two examples the optical signal levels can be improved by manipulating the spectral LSP resonance position of the particles. This finding triggered the search for a method allowing optical particle tuning.

Part II of this thesis describes an approach which allows such a spectral LSP manipulation on the single-particle level. The method makes use of the optically induced reduction of metal salt complexes in solution, which leads to the deposition of thin layers of elemental metal onto single, intentionally addressed particles. The deposition process is monitored by optical LSP analysis, and thus the tuning of the optical particle properties is controlled in situ.

With this technique, a manipulation of both the size and the shape of single nanoparticles was achieved. Initial experiences were gained by manipulating spherical and ellipsoidal gold particles, for which a red- and a blueshift of the LSP resonance was observed, respectively. The insights obtained from these experiments were then applied to tune the interparticle separation in nanoparticle pairs, i.e., to tune the resonance wavelength of these plasmonic nanoresonators. Subsequently, single resonators were used to reshape the fluorescence emission spectrum of organic molecules.

Besides size and shape, also material parameters such as the surface roughness and the surface material composition influence the optical

properties of MNPs. Both aspects are addressed using the example of rough platinum spheres and demonstrating the fabrication of bimetallic core-shell particles. As the material composition of particles not only influences their optical, but for example also their catalytic or magnetic properties, photochemical metal deposition with in-situ optical LSP read-out builds a bridge to other fields of nanoscience. The presented method is a versatile tool for the fabrication and manipulation of nanostructures, and it is not limited to the field of plasmonics.

Anne Kotiaho

Gold Nanoparticle-Chromophore Systems: Assembly and Photophysical Interactions

Tampere University of Technology, Finland
Supervisor: Prof. Helge Lemmetyinen

Gold nanoparticle-chromophore systems were prepared using two assembly strategies: thin films and functionalization of the metal cores with chromophores. These assemblies were studied with steady-state and time-resolved spectroscopic techniques and the thin films also with photoelectrical and microscopic methods.

Controlled assembly of gold nanoparticles and chromophores into solid structures is necessary for building photoactive devices but the design of applications relies on knowledge of photoinduced processes within the gold nanoparticle-chromophore systems. Alternating thin films of gold nanoparticles and chromophores were prepared using Langmuir-Blodgett and – Schäfer techniques. The photoelectrical measurements indicate that the particles can function either as electron acceptors or donors to the photoexcited chromophores, demonstrating the active role of the gold cores in photoinduced charge transfer reactions in films. Photoinduced electron transfer takes place from a poly(hexylthiophene) layer to an adjacent gold nanoparticle layer, and in the case of a porphyrin or a fullerene layer, the gold nanoparticles donate electrons to these chromophores. While photoelectrical measurements demonstrated charge transfer in the films of porphyrins and gold nanoparticles, also

energy transfer was considered to be possible. Time-resolved spectroscopic measurements showed that most, more than 80%, of the photoexcited porphyrins decay by energy transfer to the gold nanoparticles, whereas charge transfer is a minor relaxation route. Both energy and charge transfer processes are known to take place in chromophore-gold nanoparticle systems and in the case of porphyrin-gold nanoparticle films the relative importances of these two processes could be estimated.

The highest photoelectrical signal was observed for films combining gold nanoparticles and porphyrin-fullerene dyads. Films of porphyrin-fullerene dyads and gold nanoparticles are a step towards the construction of both structurally and functionally more complex systems. Porphyrin-fullerene dyads are known to undergo intramolecular photoinduced charge transfer via an exciplex intermediate state. Certain type of porphyrin-fullerene dyads can organize in Langmuir films, and thus the porphyrin moieties of the dyad are located on their own plane adjacent to the plane formed by the fullerene moieties. A gold nanoparticle layer enhances charge transfer of the dyad significantly, when placed near the porphyrin moieties of the dyads. In addition, fluorescence measurements indicated that the adjacent gold nanoparticle layer affects the relaxation of the exciplex state of the dyad.

The thin film strategy followed was successful in organizing the particles and chromophores at close distances. The way to control even better their organization is to attach the chromophores directly to the metal core surface. Porphyrin- and phthalocyanine-functionalized gold nanoparticles were prepared using a ligand exchange method. Photoexcited porphyrins transfer energy very rapidly, in few picoseconds, to the gold cores as shown by time-resolved fluorescence measurements. The packing of the porphyrins on the gold nanoparticle surface and their fluorescence lifetimes are dependent on position of the linkers on the porphyrin molecule.

The phthalocyanine-functionalized gold nanoparticles offered a possibility to study the photoinduced processes in more detail because both of the components could be excited nearly selectively. Time-resolved absorption measurements were used to study their fast photoinduced processes. Selective excitation of the phthalocyanines leads also to electron transfer to the gold cores, and most likely also to energy transfer. The role of gold cores as energy acceptors in chromophore-functionalized gold nanoparticles has been widely

studied and reported, whereas observations of gold cores acting as electron acceptors are few. Selective excitation of the gold cores in phthalocyanine-functionalized particles results in energy transfer to the phthalocyanines, demonstrating that the gold cores can behave as energy donors.

These results show that although the photoinduced processes of gold nanoparticle-chromophore systems are generally known, they are strongly affected by the choice of the chromophore and by the design of the system. The next step in assembling chromophores and gold nanoparticles would be to organize functionalized gold nanoparticles into solid structures. These systems offer many possibilities for controlling organization and thus the rates of photoinduced processes. Tunable parameters could include, for example, size and choice of the metal nanoparticle, choice of the chromophores, orientation and distance of the chromophore relative to the metal core and excitation energy. The gold nanoparticle-chromophore systems are a fragment of the booming area of nanotechnology that is and continues to develop, more and more as a part of everyday life and not just something from the pages of science fiction books.

François-Alexandre Miannay

Spectroscopic study of the interaction between UV light and guanine-rich DNA sequences

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Supervisors: Prof. Dimitra Markovitsi and Prof. Thomas Gustavsson.

It is well established that absorption of UV radiation by DNA induces photochemical reactions that ultimately may lead to carcinogenic mutations. Although the final photoproducts associated with the DNA lesions are well characterized, the fundamental processes at the origin of the photodegradation are not yet understood. The aim of this thesis was to characterize the singlet excited states of guanine-rich DNA strands. No detailed spectroscopic information was available for such systems prior to the present work.

The thesis begins with an in-depth study of the photophysical properties of the monomeric chromophore dGMP (2' deoxyguanosine 5' monophosphate) [1]. Subsequently, two different types of DNA secondary structures containing GC base pairs are studied. This part starts with double helices having an alternating sequence (GC and ATGC) [2]. For comparison, natural DNA double helices with randomized sequences. Finally, G-quadruplex structures formed by association of four oligonucleotides d(TGGGGT) are studied [3]. All studies were performed in aqueous solution using optical spectroscopy. The excited states relaxations dynamics, as manifested by time-resolved fluorescence, were followed over a very large time scale (from 100 femtoseconds to 100 nanoseconds) by combining the two techniques "fluorescence upconversion" and "time correlated single photon counting". It is worth noticing that the fluorescence quantum yields of the DNA components studied are on the order of 10^{-4} , making these experiments particularly delicate.

To resume, the comparison between monomeric chromophores and DNA multichromophoric systems led to the conclusion that the Franck-Condon excited states are delocalized and subject to ultrafast (<100 fs) energy transfer between the bases. It was also demonstrated that, contrary to the monomers, double and quadruple strands possess long lived emitting states, characteristic for "forbidden" transitions. Interestingly, the "normal" fluorescence, corresponding to allowed transitions, decays more rapidly for GC double strands than for G-quadruplexes whereas the opposite is observed for the "forbidden" transitions. Finally, the theoretical prediction that GC base pairs would act as energy sinks in photoexcited DNA double strands was examined. It was shown that GC base pairs may act as "partial" energy sinks for the excited states involved in the strong fluorescence (short-lived but allowed transitions), but they cannot be considered as "absolute" energy sinks as evidenced by the existence of a non-negligible contribution of weaker fluorescence ("forbidden" but long lived transitions) emanating from high-lying excited states [4]. The exact nature of these highly situated excited states remains to be determined.

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Marja Niemi

Photoinduced Electron Transfer in Dyads and Triads of Porphyrins, Phthalocyanines and Fullerenes

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Supervisor: Prof. Helge Lemmetyinen

Developing environmentally sustainable solutions to the increasing energy demand of the world is one of the most important goals of research. The ultimate renewable energy source is the sun, which emits more than enough (120 000 TW) energy onto Earth to cover the current energy need (13 TW) completely. The reason why solar energy is utilized to a much lower degree (2 GW) than possible is the lack of inexpensive and efficient technology for the purpose. Mimicking nature's complex photosynthesis system in detail is not feasible, but a simpler approach needs to be taken. The essential tasks of the system are light harvesting and electron transfer. Thus the

simplest mimic is a dyad molecule consisting of an electron donor (D) and an electron acceptor (A) with at least one of the moieties being able to absorb the light.

In photosynthetic reaction centres the chromophores are held together in a membrane by a protein. In the artificial systems the close contact between the electron donor and acceptor is usually achieved with a covalent linker joining the chromophores. A single linker can either be rigid, keeping the donor and acceptor in fixed orientation, or flexible, allowing the chromophores some freedom to move with respect to each other. In either case an advantageous symmetric structure with face-to-face orientation can be difficult to obtain. To realize a more stable, symmetrical dyad structure, two-linker strategies have been developed. Such dyads have also been modified to form solid films in which the molecules are oriented controllably. This is of special interest for application in photovoltaic devices such as solar cells.

In this study both dyad and triad structures were studied. Porphyrins and phthalocyanines were selected as the electron donor part of the molecules. Fullerene was used as the acceptor in all the compounds. The two-linker approach was followed in both the dyad and triad molecules. Focus of the study was on detailed determination of the reaction schemes for the compounds after photoexcitation using mainly time-resolved spectroscopic methods. The desired efficient ET was achieved in all of the studied compounds and the increase in the CS distance in the triads compared to corresponding dyads resulted in a longer-living CS state. The phthalocyanine-fullerene dyads were found to behave similarly to the previously studied porphyrin- and phytychlorin-fullerene dyads with comparable organization of the donor and acceptor, i.e. the ET reaction proceeds via an intramolecular exciplex. The triad structures were also studied in solid state examining specially the possibility of using the compounds in photovoltaic applications. Enhancement of both photovoltage and photocurrent generation was observed, compared to the corresponding porphyrin-fullerene dyad samples, as was expected on the basis of the study of the triads in solutions.

Photoinduced electron transfer of several dyads and triads, consisting of porphyrins or phthalocyanines as electron donors and fullerene as acceptor, was studied. Efficient electron transfer was observed in the studied compounds due to two important approaches in the design of the molecular structure: (i) appropriate selection of the donor and

acceptor moieties and (ii) controlled orientation and distance of the moieties achieved with two covalent linkers connecting the donor and acceptor.

Mainly spectroscopic methods were used to determine the reaction schemes of the photoinduced reactions. Time-resolved spectroscopy revealed the transient states of electron transfer and it was confirmed that the intermediate exciplex state precedes the charge-separated state in all the studied compounds. Rate constants of the transitions and energies of the states were evaluated in both polar and non-polar solvents.

To test the possibility to use the studied compounds in solid state photovoltaic devices, thin films with porphyrin-porphyrin-fullerene triad structures were attached on glass substrates covered with a transparent indium tin oxide layer. The triad structures were obtained by building successive self-assembled monolayers (SAM) of porphyrin and porphyrin-fullerene dyad on top of each other. Because of the presence of the secondary electron donor, the triad structures were found to enhance both photocurrent and photovoltage generation compared to the corresponding porphyrin-fullerene dyad SAM.

The following conclusions can be drawn based on the reported results:

1. Photoinduced electron transfer of the various phthalocyanine-fullerene dyad and porphyrin-porphyrin-fullerene triad compounds studied was found to be very efficient even in a non-polar solvent, such as toluene. The rapid electron transfer reactions observed in all the compounds are consistent with the symmetric, double-linker design strategy of the molecular structures.
2. Attaching a side porphyrin unit to the previously studied porphyrin-fullerene dyad to form a triad molecule resulted in the expected prolongation of the lifetime of the charge separated state.
3. The inner porphyrin and fullerene of the studied triads were found to act as a unit behaving in the same manner as in the corresponding dyad molecules, e.g. forming an exciplex with distinct emission in non-polar solvent.
4. Consistently with the studies of the triads in solutions, the photovoltaic behaviour of solid monolayer film samples of Zn porphyrin-free-base porphyrin-fullerene triads is improved considerably compared to the corresponding dyad films due to the higher absorbance and the longer charge separation distance.

5. The phthalocyanine-fullerene dyads follow the same general reaction scheme of photoinduced electron transfer as the previously studied porphyrin- and phytychlorinfullerene dyads. The scheme includes an intermediate exciplex state preceding the charge-separated state.

6. Because of the rapid electron transfer forming the charge-separated state in the phthalocyanine- fullerene dyads, the characteristic exciplex emission is quenched efficiently and observed only weakly in the steady state emission spectra.

Gabriela Petroselli

Photosensitized oxidation of purine nucleotides by pterin in aqueous solutions

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Supervisor: Prof. Andrés Thomas

In this doctoral thesis we investigated the photosensitization of 2'-deoxyadenosine 5'-monophosphate (dAMP) and 2'-deoxyguanosine 5'-monophosphate (dGMP) by pterin (PT) in aqueous solution under UV-A irradiation.

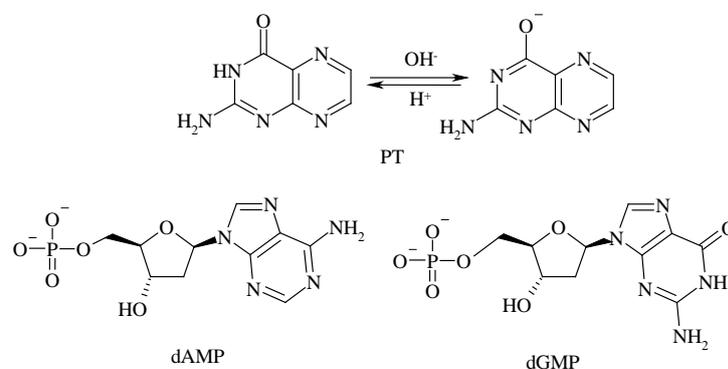


Figure 1: Molecular structure of PT, dGMP and dAMP

Solar radiation induces modifications to genomic DNA and is implicated in the induction of human skin cancers. UV radiation is the most mutagenic and carcinogenic component of the solar radiation. UV-B radiation (280-320 nm) damages DNA through the

direct excitation of the nucleobases. On the other hand, although nucleobases absorb very weakly above 320 nm, UV-A radiation (320-400 nm) may damage DNA through photosensitized reactions.¹ This indirect action is mediated by a photosensitizer (endogenous or exogenous) which is excited by the UV-A radiation.

The chemical changes in DNA and its components resulting from photosensitized reactions can take place through different mechanisms. It has been demonstrated that energy transfer from the triplet state of the photosensitizer to pyrimidine bases leads to the formation of pyrimidine dimers.¹ Photosensitized oxidations also contribute to DNA damage induced by UV-A radiation. These processes involve the generation of radicals (type I), *e.g.*, *via* electron transfer or hydrogen abstraction, and/or the production of singlet molecular oxygen (¹O₂) (type II).²

Pterins, heterocyclic compounds widespread in biological systems, are derived from 2-aminopteridin-4(1*H*)-one or pterin (PT) (Fig. 1). Several pterin derivatives participate in important biological processes such as the synthesis of amino acids and nucleobases, nitric oxide metabolism and the activation of cell-mediated immune responses. Pterins behave as weak acids in aqueous solutions, the dominant equilibrium at pH > 5 involving an amide group (acid form) and a phenolate group (basic form) (Fig.1, p*K*_a = 7.9 for PT). The participation of pterins in photobiological processes has been suggested or demonstrated in the past decade, and interest in the photochemistry and photophysics of these compounds has subsequently increased. Under UV-A excitation, these biomolecules can fluoresce, undergo photooxidation to produce different photoproducts and generate reactive oxygen species such as ¹O₂.³ Interestingly, some pterin derivatives (*e.g.* bipterin, 6-formylpterin, 6-carboxypterin) accumulate in the skin of patients affected by vitiligo, a depigmentation disorder, where protection against UV radiation fails due to the lack of melanin.⁴

The capability of pterins to photoinduce damage to DNA was demonstrated for the first time in 1997.⁵ Taking into account indirect evidence, the mechanism involved in this process was proposed to be an electron transfer with the subsequent formation of the guanine radical cation and a pterin radical anion. Later studies provided additional evidence on the photosensitizing capability of pterins.^{6,7} On the other hand, in a very recent work, photosensitization *via* ¹O₂

has been reported as the main mechanism responsible for the photoinduced cleavage of plasmid DNA by pterins.⁸

SUMMARY OF RESULTS

1-The nucleotides dGMP and dAMP deactivate ¹O₂ with different efficiency and through different mechanisms.

The quenching of ¹O₂ by dGMP is mainly a chemical process. Within the experimental error, the values of the rate constant of ¹O₂ total quenching by dGMP (k_t (1.7 ± 0.1) $\times 10^7$ M⁻¹ s⁻¹ and (8.5 ± 0.6) $\times 10^7$ M⁻¹ s⁻¹ in acidic and alkaline media, respectively) are similar to the values of the rate constant of the chemical reaction between ¹O₂ and dGMP in the corresponding media (k_r (1.7 ± 0.3) $\times 10^7$ M⁻¹ s⁻¹ and (9.6 ± 0.8) $\times 10^7$ M⁻¹ s⁻¹, respectively). It is noteworthy that the reactivity of dGMP toward ¹O₂ is much higher in alkaline media. This fact can be explained on the basis of charge effects as a consequence of the different acid-base equilibria of the nucleotides in H₂O. At pH 10.5, the guanine moiety is deprotonated at its lactam group. Since the attack of ¹O₂ takes place onto the guanine moiety, its deprotonation must be responsible for the high increase of the k_r value with the pH. On the other hand, in the case of dAMP, the physical quenching predominates and the contribution of chemical reaction is negligible ($k_t^{\text{dAMP}} = (4.1 \pm 0.4) \times 10^5$ M⁻¹ s⁻¹, $k_r^{\text{dAMP}} = (8 \pm 3) \times 10^3$ M⁻¹ s⁻¹).

2-Pterin is able to photosensitize dAMP and dGMP in aqueous solutions under UV-A irradiation. The rate of the reaction and the mechanisms depends on the nucleotide and the value of pH.

When an aerated solution containing dAMP and the acid form of PT was exposed to UV-A radiation dAMP was consumed, whereas the photosensitizer (PT) concentration did not change significantly.

During this process, O₂ was consumed and H₂O₂ was generated. A significant increase in the consumption of dAMP was observed when superoxide dismutase was present in the solution. This enzyme catalyzes the conversion of superoxide anion (O₂^{•-}) into H₂O₂ and O₂. This result suggests that elimination of O₂^{•-} inhibits a step that prevents the photoinduced oxidation of dAMP. Moreover, it was demonstrated that ¹O₂ does not participate in the photosensitization of dAMP by PT.

Two products formed during the photosensitization of dAMP were identified by ESI mass analysis: 8-oxo-7,8-dihydro-2'-deoxyadenosine

5'-monophosphate (8-oxo-dAMP) and a "product 2" (Fig. 2). 8-Oxo-7,8-dihydro-2'-deoxyadenosine (8-oxo-dAdo) has been proposed as a product of the photosensitized oxidation of 2'-deoxyadenosine (dAdo) in DNA *via* a type I mechanism.⁹ Therefore, the results support the hypothesis of an electron transfer from dAMP to excited PT. The MS/MS spectra of "product 2" suggests that a $-\text{OP}(=\text{O})(\text{OH})\text{O}-$ bridge has been formed between the phosphate and the C8 of the adenine moiety (Fig. 2).

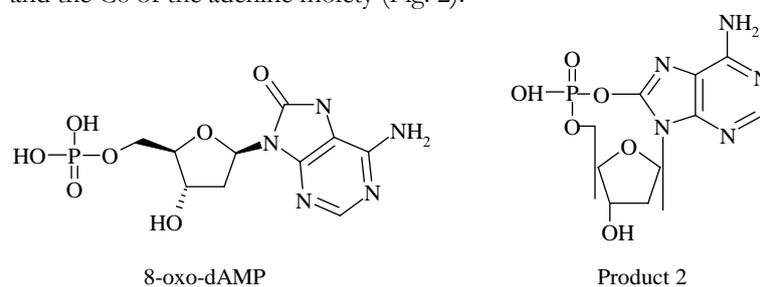


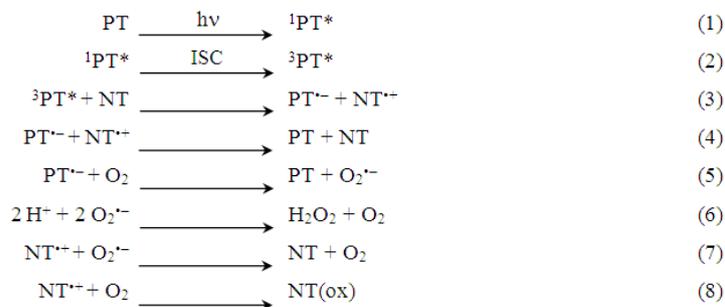
Figure 2: Molecular structure of oxidation products of dAMP.

In contrast, no evidence of a photochemical reaction induced by the basic form of PT was observed. No spectral changes and no decrease of the dAMP concentration were detected in experiments carried out at pH = 10.5. Photosensitization was not observed even at relatively high concentration of dAMP (1 mM) and long irradiation times (more than 2 hours). Probably, the process of electron transfer from the nucleotide towards PT is less efficient for the alkaline form than for acid form because PT is negatively charged at 10.5. Another factor to consider is the dismutation of $\text{O}_2^{\bullet-}$ in H_2O_2 and O_2 and their dependency with the pH. The $\text{O}_2^{\bullet-}$ is consumed mainly through its protonated form HO_2^{\bullet} (pKa = 4.85). Therefore, in the acidic media the lifetime of $\text{O}_2^{\bullet-}$ is smaller than in the alkaline media. Then at pH 10.5 the reaction between $\text{dAMP}^{\bullet+}$ and $\text{O}_2^{\bullet-}$ could contribute significantly to avoid the consumption of dAMP.

When aerated solutions containing dGMP and PT at pH 5.5 are exposed to UV-A radiation, dGMP is consumed, whereas the photosensitizer (PT) concentration does not change significantly. During this process, O_2 is consumed, H_2O_2 and highly polar compounds are generated. Additionally, $\text{O}_2^{\bullet-}$ acts as an inhibitor of the process. The role of $^1\text{O}_2$ in the oxidation of dGMP

photosensitized by PT was evaluated from kinetic calculations taking into account the values obtained for k_r (*vide supra*) and from comparative photolysis experiments performed in H₂O and D₂O. Results showed that the chemical reaction between dGMP and ¹O₂ does not contribute significantly to the photosensitized oxidation of dGMP by the acid form of PT (pH 5.5), thus suggesting the participation of a type I mechanism under these pH conditions. Direct evidence of electron transfer between dGMP and excited PT was obtained in acidic media by laser flash photolysis experiments showing the presence of the dGMP radical after excitation of PT at 355 nm. The formation of such a radical occurs within a time window of a few microseconds, which indicates the participation of the PT triplet state in the process. Kinetic calculations showed that despite dGMP is able to deactivate singlet excited state of PT (¹PT*), this is not involved in the electron transfer. This result suggests, that the PT triplet state (³PT*) is in charge of this process. This hypothesis was finally confirmed comparing experiments of quenching of the luminescence of ¹O₂ by dGMP in which reference photosensitizers and PT were used. The interaction between the triplet excited state (³PT*) and dGMP was confirmed by analysis of Stern-Volmer.

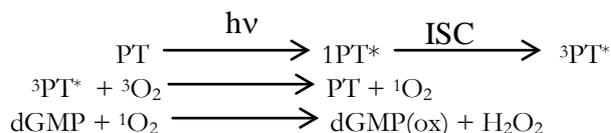
Taking into account the results obtained with dAMP and dGMP, the following general mechanism can be proposed for the oxidation of purine nucleotides photoinduced (NT) by PT in acidic media:



After excitation of PT and formation of its triplet excited state, ³PT* (Reactions 1 and 2), electron transfer between the nucleotide (NT) and ³PT* leads to the formation of the corresponding radical ions, PT^{•-} and NT^{•+} (Reaction 3). In the following step, the radical ions may recombine (Reaction 4), which explains the absence of substrate

consumption under anaerobic conditions. Alternatively, the electron transfer from $PT^{\bullet-}$ to O_2 regenerates the sensitizer and forms $O_2^{\bullet-}$ (Reaction 5). This radical disproportionates with its conjugated acid HO_2^{\bullet} to form H_2O_2 (summarized by Reaction 6) or react with NT^{++} to regenerate the substrate (Reaction 7). Finally a group of processes, represented schematically by Reaction 8 and that include the reactions of NT^{++} and its deprotonated form ($NT(-H)^{\bullet}$) with O_2 and H_2O , leads to the oxidation of the nucleotide and consumption of O_2 .¹⁰

The nucleotide dGMP, unlike dAMP, is photosensitized by PT in alkaline media. During the reaction dGMP and O_2 are consumed, the PT concentration remains constant and H_2O_2 and several polar products of the oxidation of the nucleotide are produced. In this case the kinetic calculations and the experiments carried out in D_2O showed that photooxidation takes place mainly *via* 1O_2 . Therefore, the mechanism proposed for alkaline media is:



Type I and type II mechanisms of the oxidation of dGMP photosensitized by PT are competitive and contribute in different proportions depending on the pH. In alkaline media, where the quantum yield of 1O_2 production by PT (Φ_{Δ}) and the rate constant of the chemical reaction between dGMP and 1O_2 (k_r) are higher than those in acidic media ($\Phi_{\Delta}^{10.5}=0.30$; $\Phi_{\Delta}^{5.5}=0.18$; $k_r^{10.5}=(9.6 \pm 0.8) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $k_r^{5.5}=(1.7 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), the main mechanism involves 1O_2 as the reactive intermediate. On the other hand, under acidic conditions, where the reaction with 1O_2 is much slower and the initial electron transfer is likely to be more efficient, the type I mechanism is the main pathway. Since this is the situation at physiological pH, it can be inferred that electron transfer should be the main mechanism responsible for oxidation of nucleotides photosensitized by PT in biological systems.

3-Deoxynucleotides are able to quench singlet excited states of pterin derivatives

Steady-state and time-resolved studies of the fluorescence of four aromatic unconjugated pterins (PT, 6-(hydroxymethyl)pterin, 6-methylpterin, and 6,7-dimethylpterin) in aqueous solutions in the presence of different nucleotides (dGMP, dAMP and 2-deoxycytosine 5'-monophosphate (dCMP)) were performed using the single-photon counting technique. The singlet excited states of acid forms of pterins are deactivated by purine nucleotides (dGMP and dAMP) *via* a combination of dynamic and static processes. The efficiency of the dynamic quenching is high, independently of the nature of the purine base of the nucleotide and of the chemical structure of the substituents linked to the pterin moiety. Analysis of the static quenching indicates that ground-state association between pterins and purine nucleotides takes place, but the formation of the corresponding complexes is significant only at relatively high reactant concentrations. The quenching of the fluorescence of acid forms of pterin derivatives by dCMP, a pyrimidine nucleotide, is slightly less efficient than the quenching by purine nucleotides and is purely dynamic. In alkaline media, the fluorescence quenching is much less efficient than in acidic media, the deactivation by purine nucleotides being purely dynamic, whereas quenching by dCMP is negligible.

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Denis Svechkarev

Synthesis, spectral properties and proton phototransfer reaction in a series of new heterocyclic nitrogen-containing derivatives and analogs of 3-hydroxychromone

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Charge and proton transfer processes are widely spread in nature. Compounds for which these processes are characteristic are actively investigated for over 50 years. 3-Hydroxychromone (3HC) derivatives, which exhibit unique physico-chemical properties as a result of the excited-state intramolecular proton transfer (ESIPT) reaction in their molecules, are subjects of extensive scientific research in this domain. Dual-band emission spectra of these compounds became a basis for development of the novel method of fluorescent analysis – ratiometric detection. The main advantage of this approach is that it doesn't require the use of external standards and reference samples. This particularity can be decisive and crucial in analysis of biological objects. Years of investigations of various possibilities for the practical application of 3HC derivatives showed them to be capable of probing solvent polarity, viscosity, and proton donor or acceptor ability. These fluorescent dyes can also be used as polypeptide markers, as well as indicators and sensors in the studies of physico-chemical properties of biological objects, for example, intracellular pH, surface electric potential of cell membranes and even for early detection of cell apoptosis.

In the past 10 years, the synthesis of 3HC derivatives with additional heterocyclic moieties was extensively developed. Thus, 3HC showing the most long-wavelength fluorescence and the highest quantum yields belong to this series of compounds. 3HC derivatives having heteroaromatic substituents in the position 2 can be considered also as systems with a potential possibility of the alternative Hydrogen bonds formation, and as a result – with a possible alternative excited state proton phototransfer pathway. This particularity opens new and

rather intriguing page in the study of the ESIPT process photophysics, and also in the design of new multi-band fluorescent compounds – highly effective ratiometric probes with the increased number of data collecting channels.

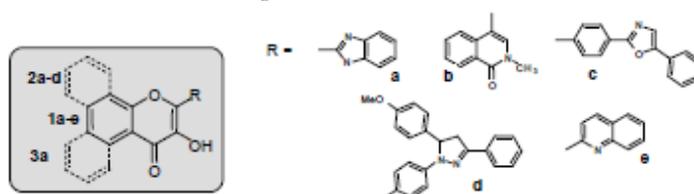


Figure 1. Heterocyclic 3-hydroxychromones under study.

In the present work, a series of the new heterocyclic nitrogen-containing derivatives and analogs of 3HC was synthesized (Fig. 1). In the investigated compounds, benzimidazole, N-methylisoquinolone, diphenyloxazole, triphenylpyrazoline and quinoline fragments were introduced in the position 2 of the parent chromone bicycle. Structures of all compounds were confirmed with ^1H NMR spectroscopy, their purity was controlled with TLC. Spectral and fluorescent properties of the title compounds, as well as their solvatochromism in a number of solvents of different nature (Table 1), and also intramolecular proton transfer reaction in their excited states were investigated (Figure 2). The Reichardt's normalized polarity index ETN was selected to investigate polarity influence on spectral behavior. Influence of the substituent nature on the spectral behaviour of the 3HC derivatives under study was analyzed.

Combining the chromone bicycle with molecular fragments being known as effective fluorophores is shown to result in the obtaining of the new highly effective multibanded fluorescent dyes exhibiting excited-state intramolecular proton phototransfer. Contrary to such behavior, strong electron acceptor substituents in the position 2 lead to significant decrease of quantum yields of fluorescence. The same effect was observed upon annealing of the benzene ring to the parent chromone bicycle.

Table 1. Spectral properties of some 3-hydroxychromone derivatives

Comp.	Solvent	ν_{obs} , cm ⁻¹	ν_1^N , cm ⁻¹	$\Delta\nu_{ST}^N$, cm ⁻¹	ν_1^T , cm ⁻¹	$\Delta\nu_{ST}^T$, cm ⁻¹	ϕ
1a	toluene	26820	24190	2630	19000	7820	0.34
	1,2-dichloroethane	26860	23140	3720	18950	7910	0.44
	acetonitrile	27180	22790	4390	18690	8490	0.65
1b	toluene	28700	23740	4960	18020	10680	0.01
	1,2-dichloroethane	30260	25485	4775	18160	12100	0.03
	acetonitrile	30380	25400	4980	18160	12220	0.04
1c	toluene	25460	22420	3040	17940	7520	0.57
	1,2-dichloroethane	25580	21520	4060	18100	7480	0.70
	acetonitrile	26020	20340	5680	18120	7900	0.51
1d	toluene	22960	20180	2780	16990	5970	0.55
	1,2-dichloroethane	22660	19060	3600	16705	5955	0.30
	acetonitrile	23380	18420	4960	16440	6940	0.48
1e	toluene	25660	22540	3120	17850	7810	0.005
	1,2-dichloroethane	25960	20880	5080	16990	8970	0.004
	acetonitrile	26100	19770	6330	16930	9170	0.003

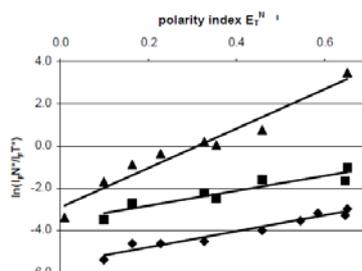


Figure 2. Dependence of the normal-to-tautomer fluorescence intensity on the solvent polarity for compounds **1a** (◆), **1c** (■) and **1d** (▲).

Introduction of a strong electron donor fragment to the position 2 of the 3-hydroxychromone significantly increased the charge-transfer character of the normal form. This makes the normal fluorescence band much more intense and increases its sensitivity to the solvent polarity. Extremely high solvatofluorochromism of the normal emission band of the compound **1d** makes it one of the most effective solvatofluorochromic dyes in the 3-hydroxychromone family. Good response of the normal-to-phototautomer ratio to the solvent polarity makes such compounds prospective for their application as ratiometric fluorescent probes. Sensitivity of their phototautomer form emission to the solvent polarity allows to keep the band separation suitable for dual-band ratiometric measurements in a wider range of solvent polarities. Our experiments proved that the proton phototransfer reaction is realized not only for the

molecules with charge transfer directed from the substituent in the position 2 to the chromone bicycle, which is traditional for this family of compounds (Figure 3, right), but also for the molecules exhibiting charge transfer in the opposite direction upon excitation (Figure 3, left).

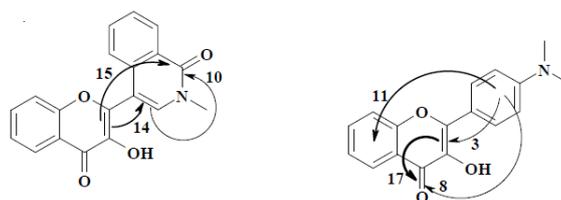
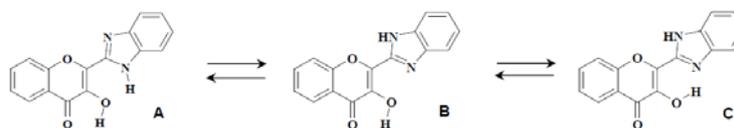


Figure 3. Electron density redistribution upon excitation in the molecules of **1b** (left) and 2-(4'-dimethylaminophenyl)-3-hydroxychromone (**DMAF**, right).

The nature of the intramolecular hydrogen bonds in the molecules of benzimidazole- and quinoline-substituted 3HC was investigated taking into account all three possible rotamers as follows:



Modeling of the possibility of an alternative intramolecular hydrogen bond formation, as well as realization of an alternative pathway for the excited-state intramolecular proton transfer reaction was effectuated. Presence of the alternative intramolecular hydrogen bonds to the nitrogen atom of the substituent's heterocycle was shown by X-ray structure analysis for both compounds in the crystalline state.

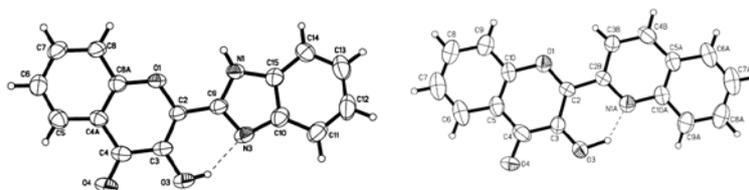


Figure 4. Structures of **1a** and **1e** in the crystalline state (XRD data).

The change of the proton transfer pathway from the “alternative” to the classical “flavonol-like” on going from crystalline state to solution was predicted for the benzimidazole-substituted derivative. At the same time, alternative H-bond appears to be stronger in the case of quinoline-substituted 3HC, thus keeping the proton transfer direction in solutions the same as in the crystalline state.

Spectral characteristics of the investigated compounds are sensitive to their environments polarity changes. This particularity make prospective to develop on their basis ratiometric fluorescent probes and sensors for various physico-chemical and medicobiological investigations. Thus, triphenylpyrazoline-substituted derivatives were shown to be useful for analysis of water or other polar admixtures in organic solvents (Figure 5), while benzimidazole-substituted 3HC could be used for water-organic solvent systems analysis in the wide range of concentrations.

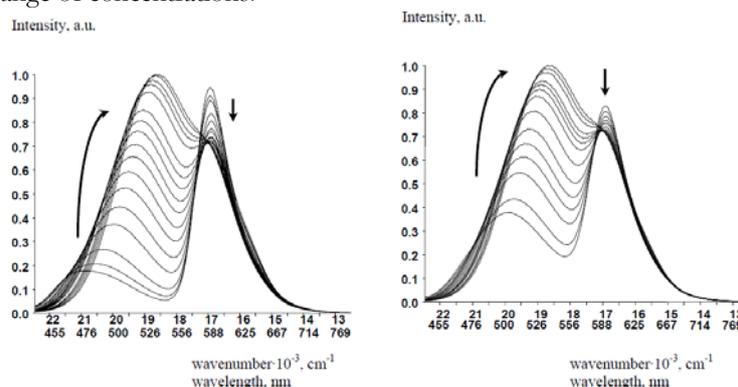


Figure 5. Fluorescence of **1d** in 1,4-dioxane (left) and acetone (right) at different water concentration (step 1% vol.).

Complex analysis of the “structure – property” dependences for the compounds under study led to the following conclusions. Combining the 3-hydroxychromone bicycle with electron donor fragments being good fluorophores allows to construct new multiband fluorescent dyes with high quantum yields of emission, good band separation, high solvatochromism and sensitivity of ratiometric response to a number of parameters of microenvironment. Further development of alternative ESIPT pathway theory can lead to the design of luminophores with increased number of emission bands, which will allow simultaneous external standard-free multiparametric probing of complex dependences, particularly in natural objects, as well as create probing systems with parallel selfcontrolled analysis of one parameter with different analytical signals.

Currently, investigations are carried out in the domain of implementation of new compounds in temperature sensing, complexation probing of heavy metals in water, fluorescence marker design, etc.

Other Theses

David Asturiol

Basis set superposition error effects, excited state potential energy surface and photodynamics of thymine

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Supervisor: Dr. Lluís Blancafort

The relaxation of thymine in the gas phase after photon absorption can be described with a multi-exponential decay.¹ This implies that there exist at least two decay mechanisms, one in the subpicosecond and another one on the picosecond time scale, that lead recovery of thymine in its ground state after the photoexcitation. The objective of this thesis has been to model the photodynamics of singly excited thymine to elucidate the decay mechanisms, using potential energy surface and dynamics calculations.

The thesis is divided in 3 parts: the first part is dedicated to find a proper level of theory for the theoretical study, that avoids the so-called basis set superposition error (BSSE) effects. The second part contains a potential energy surface and semiclassical dynamics study which shows the role of a conical intersection between the ground and the excited state in the decay, and the population of the (n, π^*) state after passage through an S_2/S_1 seam of intersection. Finally, the third part contains a quantum dynamics study of the photophysics, focusing on the passage through the S_2/S_1 seam of intersection and the relation between dynamics and seam topography.

(1) *Global and local basis set superposition error (BSSE) effects on the nucleobases.* Correlated methods such as Configuration Interaction with Single and Double excitations (CISD) and Møller-Plesset perturbation up to second order (MP2) cannot describe the planar structure of benzene with some of Pople's basis sets. A benchmark study has been performed to determine if thymine and the remaining nucleobases can also suffer from such pitfalls. Our results show that this is the case when Pople's basis sets are used in conjunction with the MP2 method. This can be explained in terms of the intramolecular BSSE, and it can be fixed by using a typical BSSE correction technique such as the Counterpoise method. However, the complete active space self consistent field (CASSCF) level used for the study of the photophysics of thymine does not suffer from this problem, and no correction is necessary.

(2) *MS-CASPT2 Minimum Energy Paths and CASSCF on-the-fly dynamics.* The photodynamics along the main decay paths of thymine after excitation to the lowest π, π^* state have been studied with multi state complete active space second order perturbation (MS-CASPT2) and semiclassical CASSCF dynamics calculations including a surface hopping algorithm (see Figure 1). The static calculations show that there are two decay paths from the Franck-Condon structure that lead to a conical intersection with the ground state. The first path goes directly to the intersection, while the second one is indirect and involves a minimum of the π, π^* state, a small barrier and a crossing between the π, π^* and n, π^* states. From the static calculations, both paths have similar slopes. The dynamics calculations along the indirect path show that, after the barrier, part of the trajectories are funneled to the intersection with the ground state, where they are efficiently quenched to the ground state. The remaining trajectories populate the n, π^* state. They are also quenched to the ground state

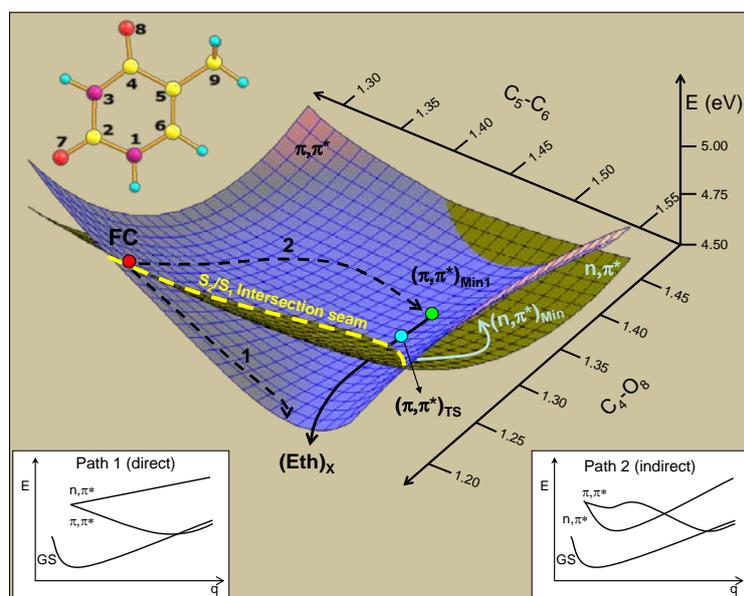


Figure 1. Two-dimensional sketch of the two lowest excited state potential energy surfaces (S_1 and S_2) of thymine in the vicinity of the Franck-Condon region.

in less than 1 ps, but the static calculations show that the decay rate of the n,π^* state is largely overestimated at the CASSCF level used for the dynamics. Overall, these results suggest that both direct and indirect paths contribute to the subpicosecond decay components found experimentally. The indirect path also provides a way for fast population of the n,π^* state, which will account for the experimental picosecond decay component.

(3) *Exploring the sloped-to-peaked S_2/S_1 seam of intersection of thymine with electronic structure and direct quantum dynamics calculations.* The role of the seam of intersection between the lowest (π,π^*) and (n,π^*) excited states in the decay of electronically excited singlet thymine has been investigated with *ab initio* CASSCF calculations and direct dynamics variational multiconfiguration Gaussian (DD-vMCG) quantum dynamics on the full-dimensional CASSCF surface, with 39 degrees of freedom. The seam has a sloped-to-peaked topography, and the dynamics at the different segments of the seam have been studied by varying the initial conditions of the propagation (see Figure 2). When

the wave packet is directed to the peaked segments, part of it traverses the seam, stays on the (π, π^*) state and heads towards decay to the ground state. In contrast to this, when the wave packet is driven to sloped seam segments it bounces back to the minimum of the (π, π^*) state. Significant population transfer to the (n, π^*) state is observed in both cases. The results suggest that a sloped-to-peaked topography can be used to control photochemical reactivity, by driving the wave packet to different regions of the seam where a different outcome of the propagation can be expected.

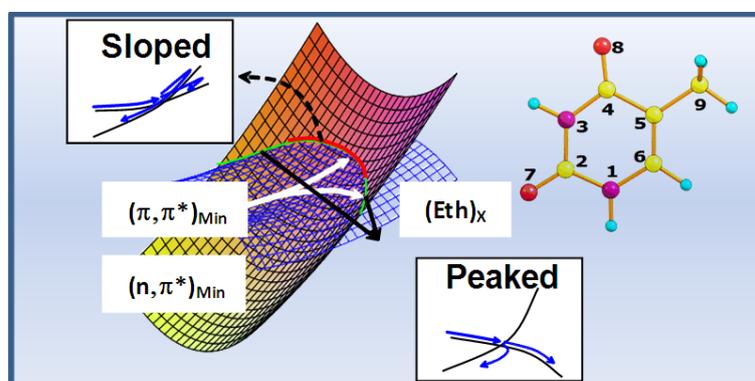


Figure 2. Sketch of the sloped-to-peaked conical intersection seam of thymine.

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Minimum-Energy Paths and CASSCF on-the-Fly Dynamics” *J. Phys. Chem. A* 2009, **113**, 10211-10218.

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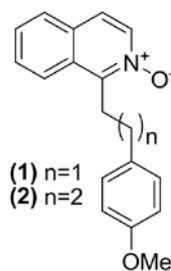
Jose-Maria Montenegro

Photoinduced electron transfer based on isoquinoline N-oxides as electron acceptors: radical oxidative processes and molecular logic switches

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Supervisors: Rafael Suau and Ezequiel Perez-Inestrosa

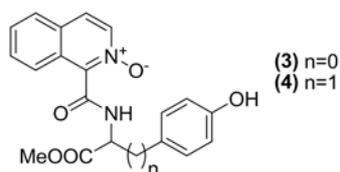
In this doctoral thesis it was presented the results of the study of the photoinduced electron transfer in a series of electron Donor (D) and Acceptor (A) moieties, linked by a Spacer (S). These systems are involved in a series of photophysical and photochemical processes including fluorescence emission and quenching and bond cleavage and formation. The A-S-D systems studied here are based on isoquinoline N-oxide as electron acceptor, 4-methoxy substituted aryl as electron Donor and an alkyl Spacer increased in length from an ethylene to a propylene chain. This way, the distance between A and D is increased to three **(1)** and four **(2)** σ_{C-C} bonds respectively.



The key step in the preparation of these compounds was the isoquinoline Reissert reaction pathway. The photophysical studies were recorded in neutral and acidic media. The emission spectra of both compounds are very similar, showing a dual-channel fluorescence emission in acidic media. Upon excitation at $\lambda_{exc} \leq 330$ nm a band at $\lambda_{em} = 380$ nm is observed, corresponding to the isoquinoline N-oxide chromophore local emission (LE). Upon excitation at $\lambda_{exc} \geq$

360 nm a second band at $\lambda_{em} = 500$ nm is observed, corresponding to the emission of a charge transfer excited state (CT). We studied the photochemical reactivity in acidic media. The photolysis of these systems leads to two main reaction products: photodeoxygenation to yield the starting isoquinoline derivative, and photohydroxylation.

We prepared the homologous series in which the spacer moiety introduces an amide bond with two main objectives: increasing the system rigidity and using the amide bond as a connection-disconnection system where the electron acceptor could be reused in consecutive reaction cycles (**3-10**). We synthesized several systems increasing the S length, always based on the structure of 1-isoquinoline-carboxamide, to obtain derivatives where A and D are located at three, four and five bonds. The key step of the synthesis of these compounds is the amide bond formation between 1-isoquinoline carboxylic acid and the corresponding amine, followed by N-oxidation.

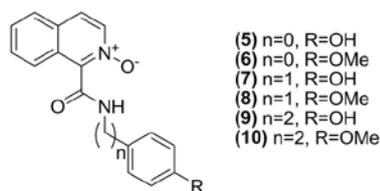


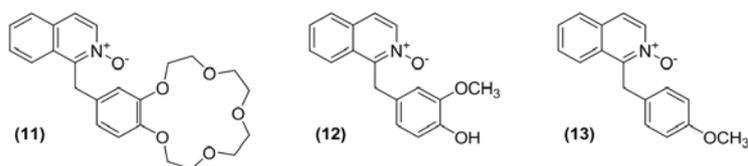
The photophysical studies of these compounds show a similar behaviour to the alkyl spacer derivatives. The emission spectra in acidic media show a dual-channel fluorescence emission.

We studied the photochemical reactivity in acidic media. The photodeoxygenation product is always found. For the irradiation of compounds, we also detect hydroxylation products in the Donor ring. This photohydroxylation is regioselective and the product obtained in both cases is the hydroxylated in ortho position to the hydroxy or methoxy group.

The changes of the fluorescence emission profile of selected compounds (called output) upon the

addition of selected chemical species (called inputs) as can be acids for N-oxide function (**11-13**), bases for phenolic moieties (**12**) and alkaline and alkaline earth metallic cations for the benzocrown ether moiety (**11**) have been studied.





These interactions produce changes in its fluorescence emission that can be studied from the Boolean logic gates point of view in order to develop molecular logic gates and switches. The changes in the fluorescence emission leads us to define INHIBIT logic gate and two more complex systems, one of them when TFA and Zn^{2+} are inputs acting over the isoquinoline *N*-oxide and the other one when K^+ and Ba^{2+} are acting over the benzocrown ether moiety.

The photophysical studies upon interaction with acid (TFA) and base (TBAH) produce four different fluorescent-emitting excited states. The Boolean interpretation of these properties leads us to define an INH and a XOR logic gate. The combination of INH and XOR, produce a Half-Subtractor logic gate. With this result, is possible to develop a reversible molecular logic system, restricted to the case where the fluorescence emission is on. This behaviour is good approach to get a totally reversible molecular system.

The photophysical properties can be defined as a demultiplexer (DEMUX). This molecular switch steers an input to one of many possible outputs. In this case, we define a molecular 1:2 DEMUX. This switch can direct the input data stream to two different output receptors, directed by a digit control "c".

Hani Salah Abdou El-Gezawy

Photophysical and Photochemical Properties of Chromophores Related to Photoactive Protein Chromophores

Mathematisch-Naturwissenschaftlichen Fakultät I
der Humboldt-Universität zu Berlin

Supervisors: Prof. Dr. Jürgen Mlynek, Prof. Thomas Buckhout

This thesis is mainly aimed to explain the photophysical and photochemical properties of several chromophores, which are related to photoactive protein chromophores.

Experimental means of UV absorption, steady state emission and time-resolved fluorescence, as well as time resolved infrared and low temperature techniques are employed in conjunction with quantum chemical calculation.

The photochemistry of several compounds depends on the donor-acceptor strength and this has been shown in the PYPE model compounds. Not only the double bond plays a role in photochemistry but also the single bond and this is tested by selectively bridged and non bridged PYPE-derivatives.

A decisive measure for classifying compounds and their photochemical activity is their position with respect to the cyanine limit (CL). The laser dye DASPI and a bridged derivative DPD-B13 have been situated beyond the CL and a corresponding frequency upshift of the IR band assigned to the double bond stretch frequency has been verified for the first time by transient infrared experiments. The CL has been tested quantum chemically for DASPI and a variety of related styrene derivatives by modelling the relevant S0 and S1 frequency differences.

The time-resolved fluorescence behaviour of the stilbene derivatives ACS, DCS and JCS is investigated in ethanol at low temperature by reconstructing the time-dependent emission spectra from time-correlated single-photon data. The correlation times for the fluorescence redshift as well as of the shape changes of the fluorescence band are slowed down in the order ACS, DCS and JCS and demonstrate an example where apparent solvation times are not independent of the solute. This finding supports the three-state model involving large-amplitude rotational motion during the excited state relaxation of ACS, DCS and JCS.

The stilbenes were compared to their larger butadiene and hexatriene analogues. The question whether a TICT state could be of importance for the photophysics of longer donor-acceptor-polyenes was answered by a comparison of the unhindered DCB with the sterically hindered dimethylated derivative DMDCB.

CONFERENCE REPORTS

CECP 2010 Conference Report

From Sunday, February 7 to Thursday, February 11, 2010, 119 photochemists from 16 different countries came together to share their results and experiences at the Congress Centre of Bad Hofgastein/Austria. It was a wonderful atmosphere and all participants really enjoyed the meeting. The scientific organization has been done by the international scientific committee: Thorsten **Bach**, Munich, Germany, Uwe **Pischel**, Huelva, Spain, Silvio **Canonica**, Duebendorf, Switzerland, Elena **Selli**, Milano, Italy, Laszlo **Biczók**, Budapest, Hungary, Xavier **Allonas**, Mulhouse, France, and Petr **Slavíček**, Prague, Czech Republic. The conference started on Sunday with the come together including a buffet and an opening lecture. **Fig. 1:**



Fig. 1: Plenary speakers of **CECP 2010**, from left to right Pérez-Prieto, Hecht, Oliveros, Vauthey (first row), Elisei, Nakatani, Bohrmann-Linde, and Tausch (second row).

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,

presented together with Claudia **Bohrmann-Linde** and Simone **Krees**), as well as short talks (28 oral presentations), and a poster session every evening (76 poster presentations). Plenary lectures have been given by Julia **Pérez-Prieto**, Valencia, Spain on photoactive nanoparticles, Stefan **Hecht**, Berlin, Germany on chemical approaches to nanoscience, Esther **Oliveros**, Toulouse, France on photochemically enhanced Fenton reactions, Eric **Vauthey**, Geneva, Switzerland on ultrafast photoinduced processes at liquid interfaces, Fausto **Elisei**, Perugia, Italy on ultrafast time-resolved spectroscopic investigations, and Keitaro **Nakatani**, Cachan, France on organic photochromic systems in the solid state.

In order to keep the scientific level of the meeting on a internationally high one the scientific committee selected 6 plenary lectures (out of 17 suggestions) and 28 (out of 40 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 Thorsten Bach) for invited speakers is also gratefully acknowledged. The local organizing committee has been formed by: Stephan Landgraf (local coordinator from EPA Austria), Sabine Richert (conference secretary), Asim Mansha, Sadia Asim, Kraiwan Punyain, Truong Nguyen Xuan, and Alexander Wankmüller. 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 Kendlbacher, tourist office. Official web site of the meeting:

www.ptc.tugraz.at/gastein

The key idea of the CECF 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, all attendees from Eastern European countries, and retired researchers could join for a reduced fee, too. The system behind this

could be seen in the budget plan of the meeting (Fig. 2). For the first time a reduced fee for EPA members has been offered (2/3 of the annual member fee). For **CECP 2012** held in second week of February, 2012, in Bad Hofgastein a small increase of the fees has to be accepted to compensate inflation.

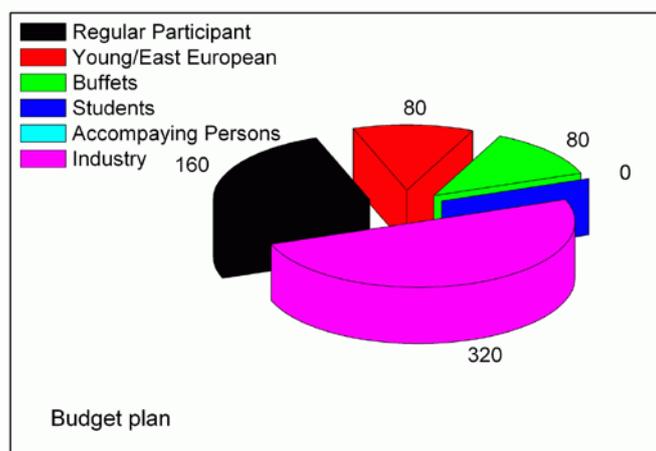


Fig. 2: Budget plan of CECP 2010 (in €) including early paying bonus.

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.

Finally 128 persons registered for the meeting till the beginning of the conference. 44 % were students (PhD not completed), 35 % were regular participants including plenary lecturers, scientific committee, and the local coordinator, 11 % were attendees from Eastern Europe and young researchers (from the rest of Europe). The latter two groups had to pay the reduced fee. The following two diagrams show the distribution of the participants of **CECP 2010** (Figs. 4,5).



Fig. 3: Congress centre of Bad Hofgastein. Photo from 2010.

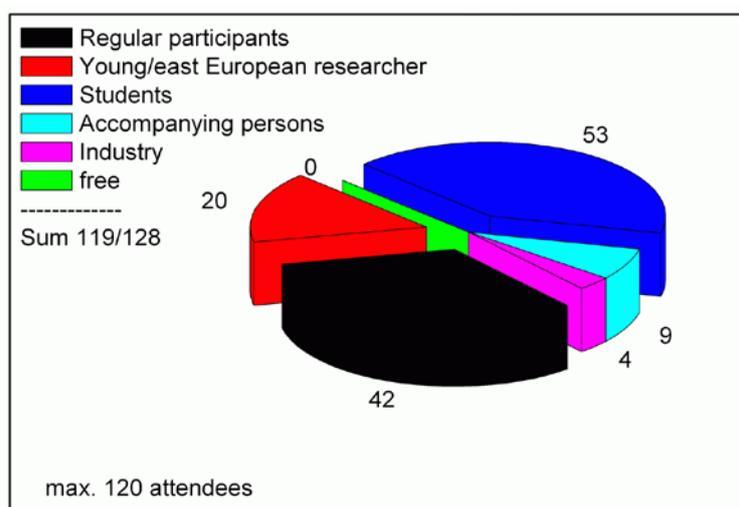


Fig. 4: Finally 119 participants arrived in Bad Hofgastein.

The income of **CECP 2010** (Fig. 4) is split into the conference fees of regular participants (42 %), from Eastern Europe and young researchers (16 %), and students (23 %). Additional funding could be obtained by the Swiss Chemical Society (6 %, via Thomas Bally, Fribourg). Receipts (in cash and in kind) from industry could also be achieved by the local coordinator (9 %). The rest to 100 % came from accompanying persons and reserves from 2008. The final negative budget has been compensated by the Austrian section of EPA.

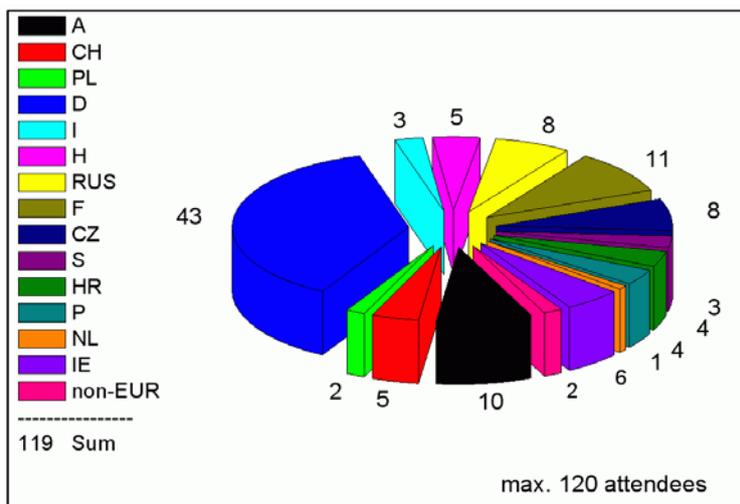


Fig. 5: Finally 119 participants arrived Bad Hofgastein sorted by country.

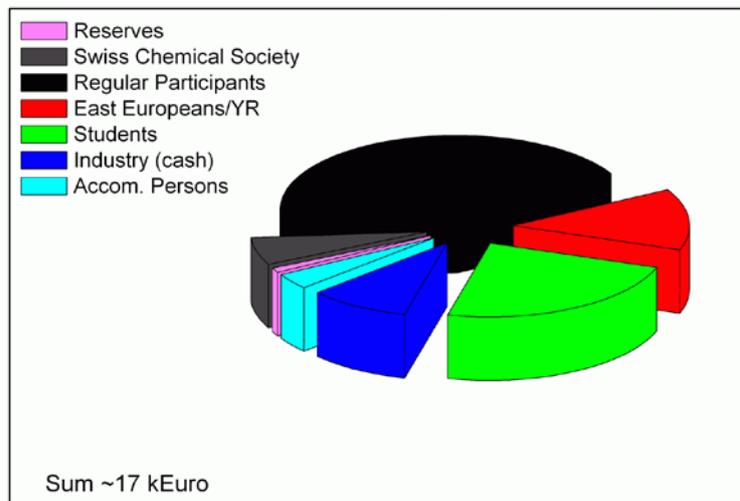


Fig. 6: Income of CECP 2010.

The expenses of **CECP 2010** (Fig. 7) were dominated by the evening buffets (51 %, real costs: 18.49 € 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 (9.5 %). Parts of it, such as coffee pots and trolley, could be used from the **CECP 2008** 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 (2.2 %, real costs: 1.04 € per person and day). Coffee, tea, and other soft drinks have been offered during the whole meeting. All costs for the book of abstracts (135 pieces), other copies, and name tags summed up to 5.7 %. 15 % could be used for travel grants for students, young researchers and persons from Eastern Europe. All travel grant applications have been accepted by the local coordinator. 20 attendees have been supported by this procedure. Statistics: USA 1, RUS 6, HR 3, TUR 1, IE: 5, I: 1, PL: 2, D: 1, H: 1. **Fig. 7:**

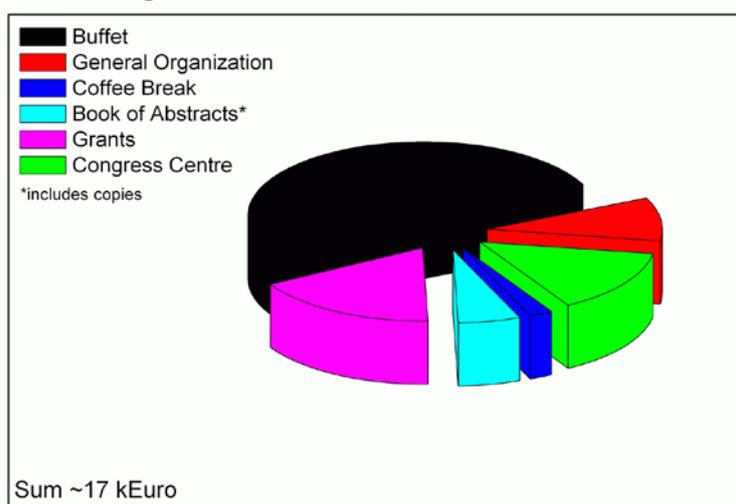


Fig. 7: Expenses of CECP 2010.

CECP 2010 Awards for Young Scientists

Additionally there are two prizes 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 prizes have been awarded by Axel

Griesbeck, Cologne at the end of the meeting prior to the conference dinner on Wednesday.

CECP 2010 Award for best oral presentation: (O9)

Simone **Draxler**, Munich/D

“Ultrafast photoreaction of fulgides and its tuning in multipulse experiments”

CECP 2010 Award for best poster presentation: (P63)

Sabine **Richert**, Graz/A

“Measurement and Numerical Simulation of Steady State and Time-Resolved MARY Spectra”

Tab. 1: Former CECP awards:

Year	Award for best oral presentation	Award for best poster presentation
2006	David Bailey , Bremen/D	Katja Draxler , Konstanz/D
2008	Dominik Wöll , Konstanz/D	David Carteau , Bordeaux/F

CONFERENCE REPORTS

Royal Society of Chemistry Photochemistry Group Early Career Researcher's Meeting 2010, Durham University

The conference **RSC Photochemistry Group – Early Career Researcher's Meeting 2010** was organised by the Chairman Dr. Gareth Williams (Durham University). This is the third such meeting, following two successful events previously. The large and continuing interest of the scientific community for this conference is demonstrated by the attendance of 51 participants. The program contained 2 plenary lectures of 40 minutes each, 13 oral presentations (15 minutes) and 21 posters.

The opening plenary lecture was delivered by Prof. Hugh Burrows of the University of Coimbra, Portugal on the topic of energy and charge migration in conjugated polymers. The session continued throughout the day with a series of short oral presentations covering a wide range of topics. Themes included solar energy (C. Linfoot), photocatalysis (J. Schneider, S. Wadhwa, C. Morton, X. Han), energy transfer (R. Evans) and novel Pt (II) complexes (J. Best, D Nolan) with applications in solar cells, crystallography (M. Warren), biochemistry (F. Dichinson, R. Arrowsmith, S. Clift) and photonic crystal fibres (G. Williams), with the majority of this work being presented by postgraduate students.

The poster session provided further opportunity for researchers from within the UK, many collaborating with groups further afield, to share and discuss their work.

The session concluded with a plenary lecture on charge photogeneration for solar energy conversion by Prof. James Durrant of Imperial College, London. An afterword included invitation to the 3rd Annual Conference on Semiconductor Photochemistry, taking place in Glasgow on April 12-16th.

Anisoara Vancea
Loughborough University

CONFERENCE REPORTS

FISPHOTON - 2nd France-Italy Symposium on Photosciences Marseille, France, December 7-10 2009

The 2nd joint meeting of the French and Italian Photochemistry groups, FISPHOTON, took place in Marseille between the 7th and 10th of December 2009, 20 years after the first French-Italian Photochemistry meeting organised in La Baume-Les-Aix, October 25-28, 1989. The meeting was under the auspices of several French and Italian scientific associations (GFP2P, GIF, SCF, SCI, CINAM, CNRS, MESR). The Chairmen of the conference were Edmond Amouyal (Laboratoire des Solides Irradiés, CEA-CNRS, Ecole Polytechnique, Palaiseau, France) and Sebastiano Campagna (University of Messina, Italy), heads of the French and Italian Photochemistry Groups, respectively. The local organisation was chaired by Arnault Heynderickx (CINAM - University of the Mediterranean Aix-Marseille II), with the help of Frédéric Fages, Marc Gingras, Olivier Margeat, Philippe Marsal and André Samat (all from CINAM, Marseille) and Isabelle Couteurier-Tamburelli (PIIM, Marseille). The actual location of the meeting was the School of Management Euromed-Marseille on the campus of the Domain of Luminy in the 9th district of Marseille. This campus is situated in the South-east of Marseille, not far from the beautiful creeks.

With about 120 participants, the FISPHOTON meeting received members from all major photochemistry laboratories in France and Italy, offering them a unique opportunity to meet and discuss science under very relaxed conditions. The atmosphere was very relaxed and both young and senior photochemists really enjoyed the event. Thanks to the sponsorship of several individuals, institutions and companies a partial financial support was attributed to many students. The meeting addressed recent developments in all areas of fundamental and applied photochemistry and photophysics as well as related photosciences. In practice, the topics presented fell into 4 broad fields: Photo-induced Synthesis, Optical Molecular Materials, Environmental Photochemistry and Solar Energy Conversion. The

scientific program included 6 plenary lectures, 11 keynote lectures and 17 oral presentations, distributed over the six half-day sessions covered by the conference. About 50 posters, displayed in the lobby during the whole conference, were presented by the Authors in two sessions.

The meeting was opened on Monday afternoon by Edmond Amouyal and Sebastiano Campagna, who made some enjoyable comparisons with the first meeting 20 years ago. The scientific sessions were introduced by Ugo Mazzucato (Perugia), who likewise expressed his satisfaction with the renewal of this meeting, even if a 20 year interval was too long in his opinion. The opening plenary talk was held by Luca Prodi (Bologna), who gave a very nice overview of the design and applications of Luminescent Silica Nanoparticles. The five other Plenary Lectures were presented by Maurizio D'Auria (Potenza) about stereochemical effects in the Paterno-Büchi reaction, Lucia Flamigni (Bologna) about conversion of light energy in multicomponent systems, Dario Bassani (Bordeaux) about molecular self-assembled architectures for molecular electronics, Jacques Delaire (Cachan) about photochemistry in microstructured reactors and Claire Richard (Clermont-Ferrand) about the photochemistry of humic substances.

11 Keynote lectures on photoprocesses in various systems were given by Paola Ceroni (Bologna, dendrimers), Ilse Manet (Bologna, G-quadruplex), Fausto Puntoriero (Messina, water splitting), Aldo Romani (Perugia, artwork applications), Elena Selli (Milano, TiO₂ photocatalysis), Salvatore Sortino (Catania, photoactive nanoparticles), Céline Croutxé Barghorn (Mulhouse, nanocomposites), Marc Verhille (replacing Céline Frochot, Nancy, photodynamic therapy), Suzanne Fery-Forgues (Toulouse, fluorescent nanofibers), Jean-Baptiste Bossa (Marseille, interstellar photochemistry) and Thomas Gustavsson (Saclay, guanine photophysics). The 17 oral presentations were given by Matteo Amelia (Bologna), Andrea Barbieri (Bologna), Giacomo Guerrini (Siena), Federico Melaccio (Siena), Luca Pretali (Pavia), Enrico Rampazzo (Bologna), Serena Silvi (Bologna), Stéphane Aloïse (Lille), Christian Beauger (Sophia Antipolis), Jean-Pierre Galaup (Orsay), Carlo Giansante (Bordeaux), David Grojo (Marseille), Jean-Pierre Malval (Mulhouse), Rachel Méallet-Renault (Cachan), Fabrice Odobel

(Nantes), Abhijit Patra (Cachan) and Mohamed Sarakha (Clermont-Ferrand). Even if the space given here does not allow a more detailed description of the scientific content of all the individual talks, it must be said is that the organisers managed to find a perfect equilibrium between Italian and French groups as well as the various main topics. In addition to the programmed oral presentations, some posters were chosen for "flash" presentations. This procedure was very instructive and generated a lot of interest and questions for the posters which were highly appreciated.

In between the scientific sessions, additional information was given regarding related topics. Sandra Monti (Bologna), representative of the European Photochemistry Association (EPA) gave an appreciated description of the recent activity of the society, undergoing a revival under the present board. Jean-Claude Micheau (Toulouse), informed on PHENICS, an international workgroup (GDR) focussing on photo-switchable organic molecular systems. Edmond Amouyal informed about an interesting one-day symposium taking place in Paris on 21st May, "Frontiers of Chemistry: From Molecules to Systems", organized by himself, SCF and Wiley-VCH, where four Noble prize winners will discuss the future of chemistry.

Edmond Amouyal concluded the meeting by underlining the success of the event, testified by the large attendance to the scientific sessions and the constructive, friendly atmosphere. Expressing a common feeling of all participants he augured that the French and Italian photochemistry groups will not wait another 20 years for the next meeting.

The FISPHOTON meeting was not all about science. Wednesday evening a magnificent dinner was given on board the "Marseillais", a sailing-ship transformed into a top-quality restaurant, located at the Old Harbour, the heart of Marseille. Special "Marsilian" fish-dishes were served together with exquisite local wines.

Thomas Gustavsson
(Laboratoire Francis Perrin, CEA-Saclay, Gif-sur-Yvette, France)
Sandra Monti
(Molecular Photoscience Group, CNR-ISOF, Bologna, Italy)

INVITATIONS

XXIII IUPAC Symposium on Photochemistry July 11th to 16th, 2010, Ferrara, Italy

Dear Colleagues,

The **XXIIIrd IUPAC Symposium on Photochemistry** will be held in **Ferrara, Italy**, on **July 11-16, 2010**. The programme consists of high quality speakers and will deal with all aspects of photochemistry and photophysics.

You can now register online and access the most recent conference information at the Symposium web site:

<http://web.unife.it/convegni/iupac-photochem-2010/>

Please take note of the following dates:

- end of early registration **April 30, 2010**
- closing date for submission of abstracts **April 30, 2010**

We are looking forward to see you all in Ferrara this summer!

Best regards,

Franco Scandola
Chair

Following an agreement with the organizers of the IUPAC Symposium on Photochemistry 2010, EPA members will pay reduced registration fees

INVITATIONS

Ciamician-Paterno' Heritage, Ferrara, Italy July 17, 2010

Dear Colleagues,

I am pleased to remind you of the meeting

Ciamician-Paterno' Heritage
Photochemical Sciences - A Look into the Future
(Ferrara, Italy, July 17, 2010)

The exciting program is available at
<http://www-2.unipv.it/photochem/heritage.htm>.

The deadline for advance registration is on May 16th.

I look forward to meet you in Ferrara.

Best wishes

Angelo Albini

Dip. Chimica Organica
v. Taramelli 10
27100 Pavia

tel +39 0382 987316

fax +39 0382 987323

angelo.albini@unipv.it

INVITATIONS

EPA at Ferrara

Dear Colleagues,

I warmly invite you to participate to the **XIIIrd IUPAC Symposium on Photochemistry** which will take place at Ferrara next July <http://web.unife.it/convegni/iupac-photochem-2010/> where EPA members benefit of the reduced registration fees.

Several important events will take place during this Symposium.

The winners of the three awards related to our Association will present their work:

- EPA Prize for the best thesis in Photochemistry: Dr Anne Kotiaho (Tampere University of Technology)
- EPA- *Photochemical & Photobiological Sciences* award: Pr Werner Nau (Jacobs University, Bremen)
- Porter Medal

At Ferrara, we will also hold our General Assembly at which I will present a report of the last three years' activities of the present Executive Committee and then, a new President and new Committee will be elected according to the EPA statutes. The General Assembly will be followed by an EPA reception offered to all members.

Closely associated to the IUPAC Symposium, a **satellite conference dedicated to Giacomo Giamician and Emanuele Paternò** will also take place (http://www-2.unipv.it/photochem/h_forward.htm). Participation is **free** for EPA members.

At this Symposium, the very essence of our discipline will be discussed; starting from its birth, continuing with future openings and tackling the way that our research becomes known to the wider public.

Dimitra Markovitsi
President of the European Photochemistry Association
<http://www.photochemistry.eu>

INVITATIONS

25th European Photovoltaic Solar Energy Conference, 6th to 10th September 2010

The **25th European Photovoltaic Solar Energy Conference** (6 - 10 September 2010) **and Exhibition** (6 - 9 September 2010) will be held at the **Feria Valencia** in Valencia, Spain.

Chairman's Message

Dear Member of the Global PV Communities,

It is my privilege and honour to invite you to participate in the **5th World Conference on Photovoltaic Energy Conversion**, which will be held in Valencia, Spain.

This World Conference on Photovoltaic Energy Conversion will bring together the three most important global scientific and strategic PV Conferences: the **25th European Photovoltaic Solar Energy Conference and Exhibition**, the **36th US IEEE Photovoltaic Specialists Conference** and the **20th Asia/Pacific PV Science and Engineering Conference**. This unique PV solar gathering will constitute the world's leading science-to-science, business-to-business and science-to-industry forum for the global PV Solar sector.



Dr. Giovanni Federigo De Santi
Director, Institute for Energy (IE)
JRC - European Commission
Conference General Chairman
<http://www.photovoltaic-conference.com/>

INVITATIONS

Solar Fuels/Photochemistry Conference 2010, 1st to 4th December 2010

The Ocean Coral, Puerto Moreles, Mexico

Leading researchers and their associates will give oral and poster presentations in all aspects of green energy chemistry. The technical areas complement one another and are as follows

1. Photophysical and Mechanistic Chemistry
2. Biosystems
3. Synthetic Molecular Systems (sensitizers, catalysts, and composite structures)
4. Semiconductor and Solid State Systems (quantum dots, films, composite structures)

The presentations will address experimental as well as computational efforts.

The top posters will be selected for additional oral presentation. There will be discussions by all attendees after the talks, at the poster session, at the conference meals and at the end of the meeting. The meeting will conclude with general remarks including the logical intellectual and programmatic foci for the following meeting

<http://www.zingconferences.com/index.cfm?page=conference&intConferenceID=77&type=conference>.

INVITATIONS

Pacificchem 2010, 15th to 20th December 2010



Promoting scientific exchange in the Pacific Basin for a healthy and sustainable future

The 2010 International Chemical Congress of Pacific Basin Societies (Pacificchem), will take place in Honolulu, Hawaii, USA, December 15 - 20, 2010. Pacificchem is sponsored jointly by the American Chemical Society (ACS), the Canadian Society for Chemistry (CSC), the Chemical Society of Japan (CSJ), the New Zealand Institute of Chemistry (NZIC), the Royal Australian Chemical Institute (RACI), the Korean Chemical Society (KCS), and the Chinese Chemical Society (CCS).

For Pacificchem 2010, The Canadian Society for Chemistry is the host society. Professor Howard Alper, University of Ottawa, is the Chair of the Congress. Professor Peter Stang, University of Utah, and Professor Kazuyuki Tatsumi, Nagoya University, are the two Congress Vice-Chairs, representing the ACS and CSJ respectively.

Pacificchem involves other Pacific Rim chemical societies in the Congress as Official Participating Organizations. Official Participating Organizations may register for Pacificchem at society rates.

Pacificchem 2010 is the sixth in the series of very successful Pacificchem Congresses. Founded in 1984, these conferences have been held in Honolulu, Hawaii, approximately every five years. Pacificchem 2010's goal is to promote collaborations among Pacific Basin chemical scientists that improve the quality of life throughout the world. It features a program highlighting such recent research contributions.

<http://www.pacificchem.org/>

INVITATIONS

Gordon Research Conference on Photochemistry, 10th to 15th July 2011

July 10-15, 2011
Stonehill College
Easton, MA

Chairs:

Cornelia Bohne & Gerald J. Meyer

Vice Chairs:

Andrei G. Kutateladze & Bern Kohler

Photochemistry has wide implications on fundamental science with technological applications that range from synthetic and mechanistic organic and inorganic chemistry to sensing/manipulation in the biological sciences to viable solar energy conversion assemblies. The 2011 Gordon Research Conference on Photochemistry will highlight recent advances on photochemical reactions, their mechanisms, spectroscopic techniques and applications to materials, organic synthesis, and biology. The conference will continue its long tradition on dynamic discussions on recent advances and unsolved scientific problems. The format of lectures, poster presentations and informal discussions provides an ideal venue for students and post-doctoral fellows to interact with the leaders in the field. These junior scientists will have an opportunity to participate in the **Gordon Research Seminar on Photochemistry** to be held prior to the GRC. The GRS will focus on photochemical aspects of solar energy conversion. A number of abstracts for posters and presentations at the GRS will be selected as short talks at the GRC.

<http://www.grc.org/programs.aspx?year=2011&program=photochem>

MEMBERSHIP APPLICATION FORM



EUROPEAN PHOTOCHEMISTRY ASSOCIATION 2009 MEMBERSHIP RENEWAL/APPLICATION FORM

Please complete the form and send it to the Treasurer by mail or fax
(do not use e-mail for security reasons!):

Dr. Silvio Canonica Eawag, W+T Dept.
Ueberlandstrasse 133, P.O. Box 611, CH-8600 Dübendorf, Switzerland
(Fax +41 44 823 5210)

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

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

Date of birth (dd/mm/yyyy): _____

If you are applying for a new membership or if your contact details have changed during 2008, please fill in the following section:

Address: (Please use your institutional address)

Tel: _____

Fax: _____

Email: _____

Membership fees for 2009 in EUR

(please check one box)

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

regular	<input type="checkbox"/> 30 EUR
student*	<input type="checkbox"/> 15 EUR * please supply attestation

For countries with economic difficulties, a reduced fee of 15 EUR can exceptionally be applied on request (only upon written approval by the Treasurer).

Alternative methods of Payment

(please fill in either 1. or 2.)

<p>1. Credit card. Please fill in the details below (all details compulsory). I, the undersigned, authorise the European Photochemistry Association to debit my credit card:</p> <p><input type="checkbox"/> MasterCard <input type="checkbox"/> Visa</p> <p>Card number _____ Expiry date: _____ For the sum of _____ EUR Amount of EUR in words: _____ Name of card holder: _____ Signature of card holder: _____ Security code: _ _ _ (this code corresponds to the last three digits to the right on the back of your credit card)</p>			
<p>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 IBAN: CH27 0025 1251 8404 5260 C</p> <p>I herewith certify that I effected a bank transfer on _____ (fill in date) for the sum of _____ EUR to cover the EPA membership fee for the year(s) 2009 - _____. Signature of the member: _____ Please ensure that you are clearly identified on the bank order.</p>			