



**European Photochemistry Association**

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# **NEWSLETTER**

**December 2011**

General information about the European Photochemistry Association

is available at:

[www.photochemistry.eu](http://www.photochemistry.eu)

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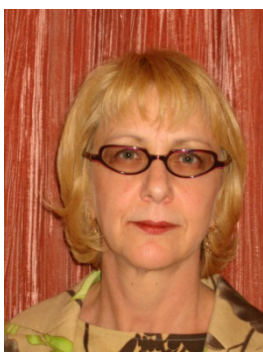
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## EDITORIAL

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### President's Letter

You may be surprised to receive this December issue of the Newsletter by the end of January. The reason for this is quite simple. As you will see while browsing this Newsletter, it contains the PhD thesis abstracts of the nine nominees for the third EPA Prize for the best PhD thesis in photochemistry. As the deadline for the nominations was December 31, we have decided to postpone the publication of this Newsletter in order to be able to present you these abstracts. It is reassuring to see that these theses have been done in laboratories located in all parts of Europe, showing that EPA is not a misnomer. A quick look at these abstracts demonstrate very clearly the large diversity of photochemical activity going on in Europe, ranging from more fundamental aspects of light/molecules interactions to potential applications in photocatalysis or photomedicine. A closer look allows realising the excellent quality of these works, and I am frankly rather happy not to be a member of the committee that will have to select the recipient of the 3rd EPA prize. The award ceremony will take place in Coimbra during the XXIV Symposium on Photochemistry. At this occasion we also have our General Assembly and the election of the President and of the members of the Executive Committee. There are thus many reasons to visit Coimbra this summer and I hope to see many of you there. Meanwhile, I think it is not too late to send you my best wishes for a happy and successful New Year.

Eric Vauthey  
EPA President

# **THE STATUTES OF THE EUROPEAN PHOTOCHEMISTRY ASSOCIATION**

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## **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**

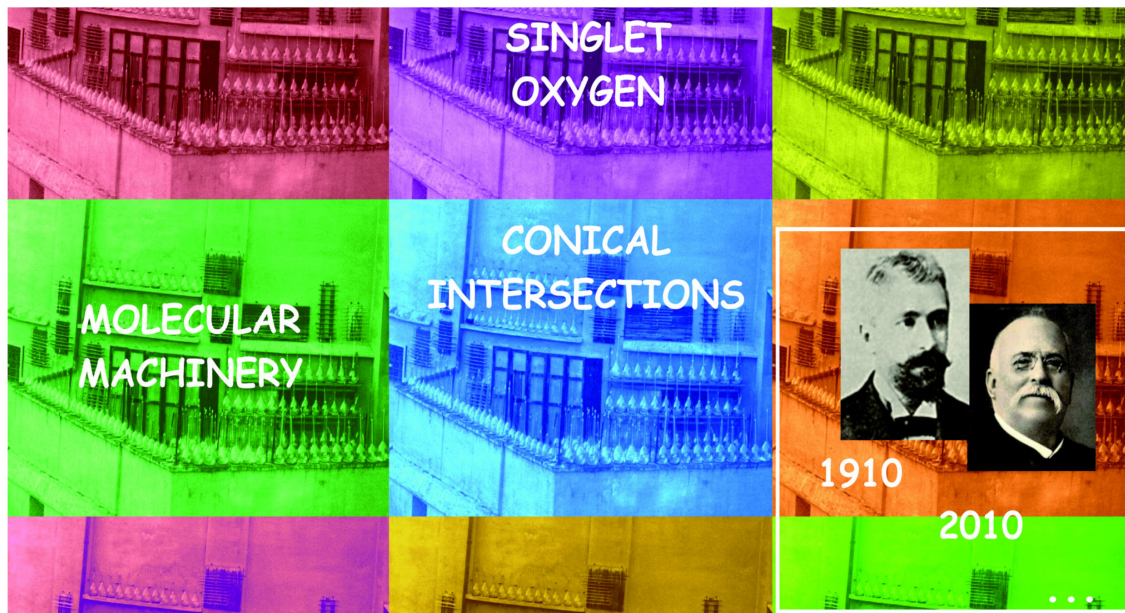
##### **ARTICLE 10**

- (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.

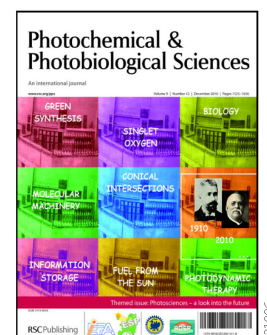
## PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



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**PERSONAL NEWS**

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**Obituary: Professor Derek Bryce-Smith**

On the 24<sup>th</sup> June 2011, Derek Bryce-Smith died at the age of 85. He was the first Chairman of the European Photochemistry Association and had a long and distinguished academic career spanning a wide diversity of scientific interests including organometallic chemistry, radical chemistry, photochemistry, environmental science, nutritional science and behavioural science. His humble scientific beginnings, however, gave no indication of the breadth and depth of chemical knowledge for which he would be later renowned. Indeed his school reports at age 13 placed him 23rd in chemistry out of a class of 26, but first place in Latin! The school report may have been the shock needed to awaken his seemingly dormant scientific abilities and interests, for he later remembered that in his early teens, he had “the overwhelming compulsion” that his career lay in chemistry not languages.

Derek left school when he was 16 and went on to South West Essex Technical College where he took a London University External Degree in Chemistry and graduated in 1945 at age 19. For the next three years, Derek worked in industry in such diverse areas as coal research and colour photography: the latter studies involved a number of unsuccessful attempts to exploit information which had been obtained on the German Agfa process at the end of the Second World War. This period was not, however, wasted and while in gainful employment during the day, Derek studied in the evenings and in his spare time at West Ham Municipal College, Stratford, for a Special Honours Degree at London University. Those of us who have followed a similar “part-time” route in our tertiary education will be well aware of the dedication and single-mindedness that such a course demands for a successful outcome.

By 1948, Derek had graduated from London University, and had turned his back on the more lucrative industrial side of chemistry. Instead he sought out the meagre existence provided by a postgraduate research studentship. Of the Professors of Organic Chemistry he contacted for such a position only Prof. C.K. Ingold responded positively but at the interview, he was surprised to hear Derek decline his offer of a studentship giving as the reason that the proposed study on nitration of nitronium tetrafluoroborate did not catch his interest and did not provide the research training he was seeking. A change of topic to the stereochemistry of mustard gas derivatives likewise held little attraction for the aspiring young postgraduate chemist. It may have been with some exasperation that Ingold and Hughes together directed Derek to Prof. Eustace Ebenezer Turner at Bedford College (London University) for Women. The beautiful location of these laboratories in Regent’s Park and the seemingly endless source of female companions no doubt contributed to Derek’s successful studies on the metallation of aromatic hydrocarbons.

In 1951, Derek was awarded his doctorate from London University, by which time he had acquired a strong and ever-increasing appetite for academic scientific studies, and in the face of stiff competition he was awarded a prestigious I.C.I. Postdoctoral Fellowship. These Fellowships had no restrictions or even directives and Derek could now pursue his studies into the chemistry of radicals: this resulted in his taking up the Fellowship at King’s College, London, with Prof. Hey, one of the leading authorities in this area at the time. Derek held the Fellowship for an extended period of four years and it was during this time that his interest in photochemistry and his concern over heavy metal pollution, which were to dominate his scientific career for a considerable number of years, grew from a common source. In his studies Derek had the need to generate ethyl radicals which he chose to do by ultraviolet irradiation of tetraethyl lead in the presence of cumene as a radical trap. From these early experiments, Derek not only developed a great respect for the extreme toxicity of lead

compounds but also demonstrated for the first time that benzenoid compounds, widely considered previously to be photostable, would undergo photoisomerization giving fulvenes: this observation provided Derek with a breakthrough into a new area of chemistry. In 1956 Derek moved to Reading University as a lecturer and set up a small research group to investigate in much greater detail the photoreactivity of aromatic compounds. The isolation and characterisation of the 2:1 photoadduct of maleic anhydride and benzene in good yield widened the international interest in organic photochemistry enormously since it not only illustrated the synthetic potential of photoadditions to aromatic rings but also provided an early example of reactions arising from excitation within a charge-transfer absorption band. The photochemistry group in Reading was now firmly established and in 1966 Derek was appointed to the newly-established Chair of Organic Chemistry at Reading. During this decade, his research group rapidly expanded until at one time comprised 15 research workers, a large group in those days, investigating the photoaddition reactions of arenes and of quinones. A high point in the mid-1960's was the simultaneous observation by the Reading group and workers at the Argonne National Laboratory in Illinois of the *meta* photocycloaddition of ethenes to the benzene ring – a process which was to be so elegantly exploited in the 1980s as the crucial synthetic step towards numerous polyquinanes by Paul Wender's group at Stanford.

In the early 1960's, a number of photochemists in Europe expressed the general desire for a formal organisation and, initially under the auspices of the Council of Europe, the European Photochemistry Association (EPA) was founded with Derek as the first Chairman. Under a succession of able and enthusiastic Chairmen and Committee Members, the Association progressed from strength to strength with membership expanding around the globe and including interests reflecting activities in pure, applied and theoretical aspects of chemistry, biology and physics. In the early days of EPA, the Royal Society of Chemistry acknowledged the importance of "photochemistry" within the chemical community worldwide and chose the subject as one of a new series of publications to be known as Specialist Periodical Reports: Derek was the obvious choice as Senior Reporter, a position he held for 25 years.

During the 1960s and 70s, Derek also held consultancies with Shell and Esso, and following a visit from Roger Adams and an extensive tour of American academic and industrial establishments, he was invited by Du Pont to be one of their two non-American consultants; the other being Sir Ronald Nyholm. He held this consultancy for six extremely interesting but exhausting years and it was towards the end of this period that his concern over heavy metal pollution of the environment grew into a major interest. Derek was at the forefront of a worldwide campaign to eliminate lead from petrol. As these matters began to consume more of his time and energies, Derek's activities, but never his lively interest in photochemistry, inevitably declined. The demands on Derek also became political but there is no doubt in the minds of many that without Derek Bryce-Smith's constant and logical approaches and the scientific arguments against the spreading of lead across the length and breadth of the planet by the motor car, it would have taken many years longer before lead compounds were stopped being added to petrol. Indeed, Derek's work and persistence with such environmental problem has led to him being described recently as "one of the greatest public health heroes of them all".<sup>1</sup> Derek's contribution to environmental chemistry was rewarded in 1984 when he was awarded The John Jeyes Silver Medal and Endowed Lectureship by the Royal Society of Chemistry. Derek's perseverance with such matters

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<sup>1</sup> G.Lean, *The Daily Telegraph*, 2011, July 30, 24.

reflected his firmly held belief that the scientist must be socially aware and responsible, and willing to confront and where necessary oppose the dogma and financial interests of the establishment. Certainly this approach did not win him many friends in the commercial sector and may indeed have been detrimental to his academic career. After retirement from the Chair of Organic Chemistry at Reading University in 1991, Derek pursued his interests into nutritional disorders, including the factors which influence foetal development, stillbirths and behavioural aspects by researching the literature and from very many discussions with medical experts in the field until ill health during 2005, finally forced him give up these activities.

Derek was a rare bred of academic who is sadly all too rare in universities. He combined style and engaging eccentricity with a truly encyclopaedic knowledge of science and a rare ability to inject enthusiasm into undergraduate and graduate students alike. The University system would now struggle to accommodate such a character who has an independence of mind, a deep social commitment and scores of ideas spreading across the spectrum of pure and applied science. Derek had an opinion about everything and was rarely lost for an amusing or incisive comment. He was, however, always the gentlemen careful not to cause offence particularly to members of the fair sex who he always refreshingly treated with old-world courteous and gallant manners that unfortunately may largely have died in many of us during the “female liberation”. Derek was truly “a man of his time” with whom I was pleased and fortunate to be associated for so many years not only as a colleague but also as a friend.

In this appreciation of Derek Bryce-Smith, I have probably emphasised the more human side of him rather than detailed his scientific achievements. The latter are evident to those who have known him or who have read his numerous publications. All too often the scientific aspects overshadowed the human being with whom I was pleased and fortunate to be associated with for so many years not only as a colleague but also as a friend.

*Andrew Gilbert*  
University of Reading

## PUBLICATIONS

## Abstracts of Theses in Photochemistry

## Luca Pretali

*Photochemistry of Fluorinated Heterocycles: Structural Modulation of the Photoreactivity*

University of Pavia

PhD Thesis: 2011

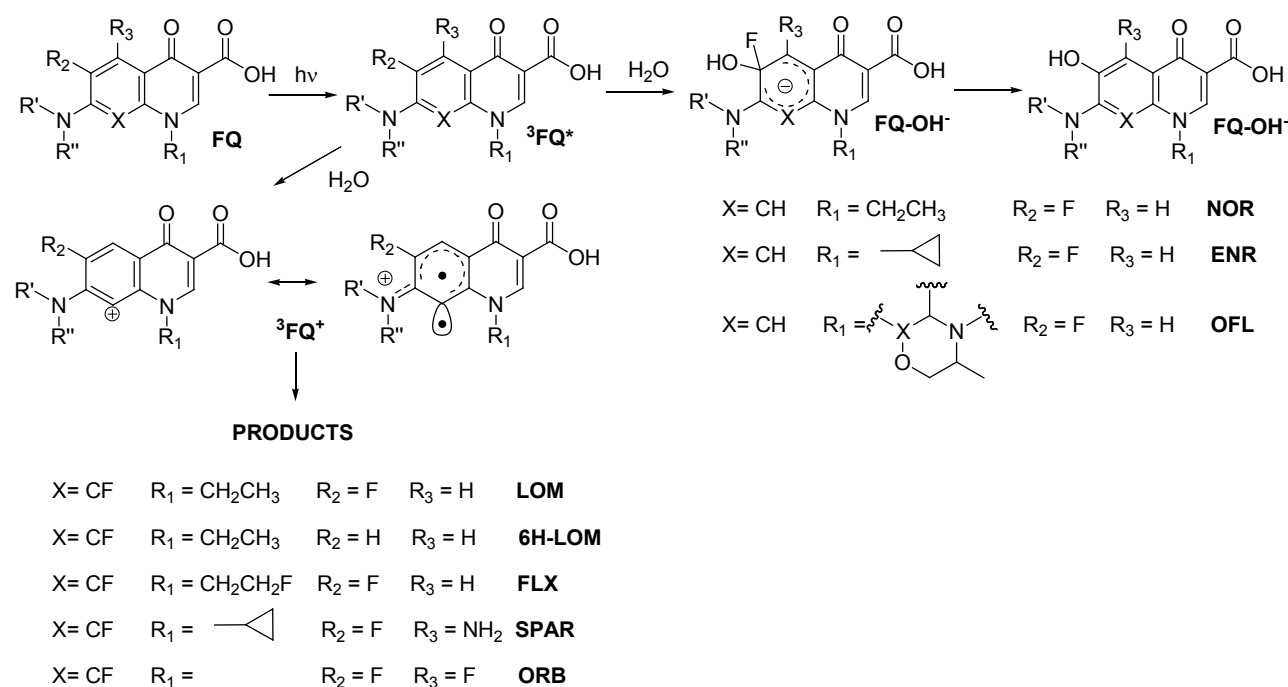
Supervisor: Dr. Elisa Fasani

This PhD project is aimed at studying the photochemistry and the photoreactivity of a variety of aromatic halides and heterocycles; these motifs are often found in the structure of antibacterial drugs (e.g. Fluoroquinolones (FQs), Oxazolidinones) and so on are of particular interest both from a chemical and a pharmacological point of view.

The research goal is to understand the innermost mechanisms that underly the photoreactivity of such compounds in order to:

- ✚ design new drugs that lack of the photochemical-induced side-effects
- ✚ exploit the peculiar photochemistry of this class of compounds in order to design a new class of photoactivable drugs that target biological substrates such as nucleic acid and DNA.

**Scheme 1.** Main primary photochemical reaction pathways for some FQs.

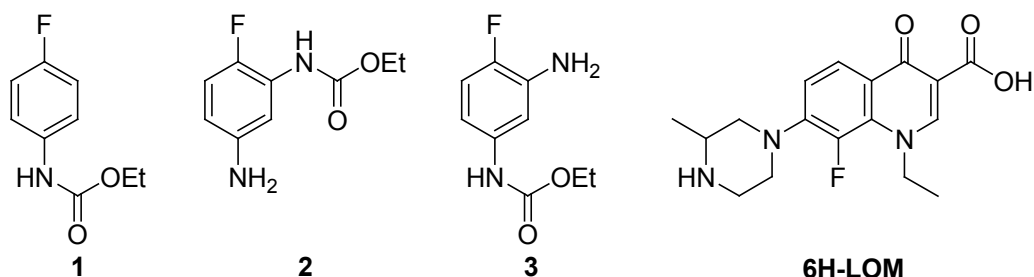


In more detail, particular attention has been paid to the study of the fragmentations from the excited state, which showed to be rather efficient and often have been shown to be the key step in actual condition<sup>1,3</sup>. It is known, for example, that the photofragmentation of the carbon-halogen bond in the excited state, is the main reactive path for a lot of these compounds (Scheme 1). This reactivity is very interesting and quite unexpected if we

consider the strength of the carbon-halogen bond ( $C_6H_5-X$  bond energies are in the order: Ar-I ( $65 \text{ kcal mol}^{-1}$ ) < Ar-Cl ( $94 \text{ kcal mol}^{-1}$ ) < Ar-F ( $124 \text{ kcal mol}^{-1}$ )).

Furthermore new model molecules have been synthesized (Scheme 2) with the aim of both correlating the structural modification introduced with the photoreactivity and the phototoxicity of these drugs and better understanding what really happens in a biological environment.

**Scheme 2.** Synthesized model molecules.

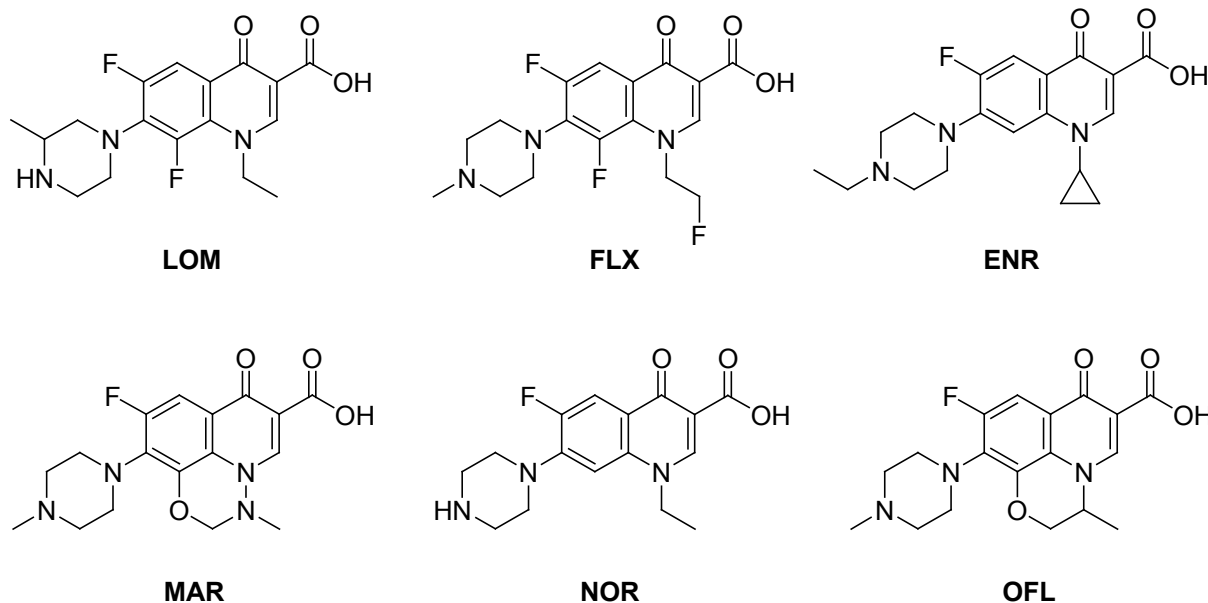


A further task was the study of the behaviour of these antibacterial compounds, used both for human and cattle, in surface waters and soils after they entered the environment, as they are known to be persistent pollutants and then potentially dangerous.

In more detail this research project has tackled in sequence:

- i. the studies on the mechanism of photoreaction of some commercial antibacterials (FQs): Lomefloxacin (LOM), Fleroxacin (FLX), Enrofloxacin (ENR) and Marbofloxacin (MAR) together with the characterization of both the photophysical and the photochemical properties of these molecules (Scheme 3)
- ii. a computational ab initio quantum mechanical study on selected molecules (LOM, NOR, OFLO, 6H-LOM) (Scheme 3)
- iii. the synthesis of new model molecules and the photochemical and photophysical studies on these new compounds, (Scheme 2).
- iv. the study of the reactivity of these molecules (LOM, FLX, NOR) in water solution in the presence of biological relevant molecules such as nucleotides (2'-desoxyguanosine-5-monophosphate, dGMP)
- v. the studies on the photochemistry of some FQs, MAR and ENR in environmental condition.



**Scheme 3. Studied FQs****Enrico Marchi***Photo- and redox-active supramolecular systems containing metal complexes***Università di Bologna****PhD Thesis: 2011****Supervisor: Prof. Paola Ceroni**

In this thesis different families of photo- and redox-active supramolecular species containing metal complexes have been studied. Following the definition given by J.-M. Lehn, supramolecular chemistry is “*the chemistry beyond the molecule, bearing on organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces*”. In a supermolecule most of the intrinsic photophysical properties of each units are expected to be maintained with relative minor changes that can be ascribed to the mutual perturbations between the units contained in the system.

The two classes of compound taken into account in this research are *metal complexes* and *dendrimers*. With the term *metal complex* we intend to refer to a compound with a central atom or ion linked in stoichiometric ratio with molecules and/or ions surrounding it. Metal complexes are fundamental constituents of living matter (for example, porphyrins in chlorophyll), and today are fundamental compounds in common life and in everyday technology. Nowadays, a lot of research is oriented towards these compounds because thanks to their versatility, stability, and outstanding properties they can work for practical applications as sensors, biological probes, electrochemiluminescent markers, emitters in organic light-emitting diodes (OLED), and solar energy conversion devices. Dendrimers are globular size, monodisperse macromolecules in which all bonds emerge radially from a central focal point with a regular branching pattern. Today dendrimers are used or are planned to be exploited in a variety of applications, taking advantage of (i) the great number of functional units that can be incorporated inside them, (ii) their tree-like structure

containing internal dynamical cavities, (iii) their well-defined dimensions close to that of important biological molecules, like proteins and bioassemblies, (iv) the presence of an internal microenvironment different from the bulk of the solution. As a result, applications ranging from the biological and medical field (artificial enzymes, drug-delivery systems, diagnostics) to nanoengineering (molecular wires, light-emitting diodes), optical data transport (fiber optics), catalysis, energy-harvesting devices and mimics of natural photosynthesis are foreseen.

The use of photochemistry for studying complex systems, such as supramolecular entities, is fundamental particularly because photochemical inputs (i.e. *light*) (i) can be switched on and off very easily and rapidly; (ii) provide the opportunity of working in a very small space and very short time domains; (iii) can be useful both to supply energy and to “read” the state of the system; (iv) allow the study of very small amount of compounds in many different conditions. Thanks to their unique excited state properties, particularly lifetimes and redox potentials, metal complexes have become irreplaceable components of supramolecular systems and, in particular, of supramolecular devices and machines that exploit light to perform useful functions. Dendrimers are the ideal supramolecular systems that can be studied with the arguments of photochemistry. Coupling luminescence with dendrimers is of particular interest since: (i) luminescence signals offer a handle to better understand the dendritic structure and superstructure; moreover, (ii) it is possible to monitor the interactions of the macromolecule with other chemical species and with the environment; (iii) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting and signal amplification for sensing purposes.

Cyclometalated Ir(III) complexes have attracted increasing interest in the last decade because of their phosphorescence properties that are ideal in view of application of these complexes in a lot of technological applications. In this thesis we report on the structural, photophysical, and electrochemical properties of two different families of bis-cyclometalated neutral iridium(III) complexes (synthesized by the group of Prof. Achille Umami Ronchi (University of Bologna)) compared to the well-known  $[\text{Ir}(F_2ppy)_2(acac)]$ . The former family of complexes contains two *ppy* or *F<sub>2</sub>ppy* ( $F_2ppy = 2\text{-(4,6-difluorophenyl)pyridyl}$ ) cyclometalated ligands and an ancillary ligand constituted by a phenol-oxazoline (*phox*), which can be substituted in the third position with a fluorine group (*Fphox*). A metal centered oxidation process and a reduction process located on the *ppy* ligand have been reported for all the investigated complexes. In addition  $[\text{Ir}(F_2ppy)_2(Fphox)]$  and  $[\text{Ir}(F_2ppy)_2(phox)]$  complexes show green-blue ( $\lambda_{em} \sim 500$  nm) luminescence with very high quantum yield in  $\text{CH}_3\text{CN}$  deaerated solution ( $\Phi = 0.8$ ). In the latter family of bis-cyclometalated Ir(III) complexes the ancillary ligand could be a chiral or an achiral *bis-oxazoline* (*box*). These complexes do not show particularly interesting photophysical properties in  $\text{CH}_3\text{CN}$  deaerated solution emitting in the green spectral region ( $\lambda_{em} = 500$  nm) with not high quantum yield ( $\Phi = 0.25$ ), but they give an interesting photoreaction when irradiated with UV light in presence of dioxygen.  $[\text{Ir}(F_2ppy)_2(4ph-box)]$  is the precursor complex that originates the most stable and interesting photoproduct. The structure of this photoproduct complex is unknown at the state of the art, but it is a strong ( $\Phi = 0.46$ ) blue emitting species ( $\lambda_{em} = 462$  nm) due to the oxidation of the precursor complex and, to the best of our knowledge, it is probably the first example of a stable blue emitting Ir(IV) complex.

As second topic three successive generations of a family of *polyethyleneglycol* (PEG)-coated Pd(II) tetrabenzoporphyrin (*PdTBP*)-based dendritic nanoprobe (synthesized by the group of Prof. Sergei A. Vinogradov (University of Pennsylvania)) are presented, and their ability to sensitize singlet oxygen and inflict cellular photodamage are discussed. It was found that the size of the dendrimer has practically no effect on the singlet oxygen sensitization efficiency, which approximates unity, in spite of the strong attenuation of the

triplet quenching rate with an increase in the dendrimer generation. Nevertheless, when compared against a commonly used singlet oxygen sensitizer, as *Photofrin*, the phosphorescent probes were found to be non-phototoxic. The lack of phototoxicity is presumably due to the inability of PEGylated probes to associate with cell surfaces and/or penetrate cellular membranes. The results suggest that protected phosphorescent probes can be safely used for oxygen measurements in biological systems *in vivo*.

Finally in this thesis a new family of two photoswitchable (**G0(Azo)** and **G1(Azo)**) dendrimers (synthesized by the group of Prof. Fritz Vögtle (University of Bonn)) with an azobenzene core, two cyclam units as coordination sites for metal ions, and luminescent naphthalene units at the periphery have been photophysically and photochemically characterized and their coordination abilities have been studied. Because of their proximity, the various functional groups of the dendrimer may interact, so that the properties of the dendrimers are different from those exhibited by the separated functional units. Both the naphthalene fluorescence and the azobenzene photoisomerization can be observed in the dendrimer, but it has been shown that (i) the fluorescent excited state of the naphthalene units is substantially quenched by well known excimer and exciplex formation and also by a very efficient energy transfer to the azobenzene units, and (ii) in the latter case the fluorescence quenching is accompanied by the photosensitized isomerization of the *trans* → *cis*, and, with higher efficiency ( $\eta \sim 0.8$ ), the *cis* → *trans* reaction. Complexation experiments performed with dendrimers **G0(Azo)** and **G1(Azo)**, both *trans* and *cis* isomers, with Zn(II) ions show that complexes of 1:1 and 2:1 metal per dendrimer stoichiometry are formed. The corresponding 2:1 metal complexes show different photophysical and photochemical properties compared to the corresponding free ligands. Practically unitary efficiency of the sensitized isomerization of *trans* → *cis* and *cis* → *trans* reaction is observed, as well as a slight increase in the naphthalene monomer emission. These results are consistent with the coordination of the cyclam amine units with Zn(II), which prevents exciplex formation. No indication of a concomitant coordination of both cyclam to a single metal ion has been obtained both for *trans* and *cis* isomer.

## **Daniel Escudera**

*Spectroscopy and photochemistry of transition metal complexes: a quantum chemical study*

**University of Jena**

**PhD Thesis: 2011**

**Supervisor: Prof., Dr. Leticia González**

Transition metal complexes possess unique chemical, photoredox and spectroscopical properties that makes them promising candidates as light harvesting antennae or photocatalytic centers in many photochemical devices, such as e.g. Ru(II) polypyridyl complexes in dye sensitized solar cells. The knowledge of the photochemical properties of these complexes is therefore of paramount importance to optimize their performance in these devices. To this aim, the computation of excited states and photochemical properties can provide useful hints to guide molecular design strategies. Unfortunately, the description of electronic excited states is still far from routine, as compared to ground state studies, and even more that of systems containing metal atoms.

The present work focuses on the computation of the spectroscopic and photochemical properties of transition metal complexes. First, a benchmark study on the excited states of a Ru(II) polypyridyl complex with quantum chemical (RASPT2) and TD-DFT methods is presented.[1] After electronic excitation, the possibilities that a molecule has for deactivating are plenty and usually such relaxation processes compete one to each other. The second main part of this thesis is then devoted to disentangling photophysical and photochemical mechanisms on several Ru(II) polypyridyl and Pt complexes with the help of quantum chemical calculations.[2,3] Thereby, some photophysical properties, such as e.g. radiative decay rates have been computed to rationalize e.g. the fine-tuning in the emissive properties.[4] These complexes are usually utilized as light-harvesting antennae in photochemical devices. In this sense, solar energy conversion is going to be of vital importance in the near future. Currently, much effort is dedicated to develop technologies which harness solar energy in an efficient manner. In this sense, there is still some place left to increase these efficiencies *via* molecular design and concomitant tune of the photophysical properties of the dyes. This is very often done in a trial-and-error manner. Instead, predictive tools would be highly desirable. To this aim, the computation of excited states and photochemical properties can provide useful hints to guide molecular design strategies. Other photochemical studies dealing with the emissive properties of Ir complexes, which are used as phosphors in organic light-emitting diodes (OLEDs), are also presented along this thesis.[5] Such knowledge can be profited in the design of new iridium complexes with optimal photophysical properties.

Due to the striking competition of radiative and non-radiative deactivation processes in many of these transition metal complexes, it is clear that the near future should be devoted to perform reaction dynamics calculations in order to get information about excited state lifetimes and estimations of quantum yields. This is still a challenge for transition metal complexes. Therefore, in this thesis, *ab-initio* excited state reaction dynamical studies have been also performed model in a small organic system, i.e. 2H-Azirines, which exhibits wavelength dependent C-N and C-C bond photoactivation.

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## **Karl Börjesson**

*Fluorescent DNA Modifications for Use as Probes of Biological Structure and as Nanotechnological Functional Units*

**Chalmers University of Technology**

**PhD Thesis: 2011**

**Supervisor: Prof. Bo Albinsson**

The first DNA base analog fluorescence resonance energy transfer (FRET) pair is presented in this thesis. It consists of the energy donor, tC<sup>O</sup> (1,3-diaza-2-oxophenoxazine), and the

energy acceptor, tC<sub>nitro</sub> (7-nitro-1,3-diaza-2-oxophenothiazine).<sup>1</sup> The base analogs are shown to be firmly stacked within the DNA helix and inflict a small or negligible perturbation on the DNA helix.<sup>2-3</sup> Both bases have their lowest lying electronic transitions well separated from higher electronic states, transitions that here are thoroughly characterized. The high fluorescence quantum yield in double stranded DNA together with the relatively strong molar absorptivity makes tC<sup>O</sup> on average the brightest ( $\Phi$ ) DNA base analog reported so far. Furthermore, the difference in quantum yields for tC<sup>O</sup> in single- and double stranded environments enables probing of local melting in nucleic acids.<sup>4</sup> The rigid placement of the base analogs, and thus transition dipole moments, results in a very high control of the orientation factor,  $\kappa^2$ , of energy transfer measurements. A set of DNA strands containing these base analogs at various positions will thus facilitate the distinction between distance and orientation information within DNA systems using FRET.<sup>1</sup>

This thesis also explores possible functions of porphyrins as photoactive functionalizations within bottom-up DNA nanotechnology. Three porphyrin nucleosides having different distances between the porphyrin unit and the nucleobase have been synthesized.<sup>5-6</sup> In presence of lipid membranes, the hydrophobicity of the porphyrin anchors, force the DNA close to the membrane surface. This creates a supramolecular assembly with the DNA in the water phase and the porphyrin in the lipid membrane phase. The porphyrin-DNA-liposome binding has been characterized and the binding orientation, depth, strength and binding site size have been determined.<sup>6-7</sup> Furthermore, lateral diffusion of large two dimensional DNA constructs anchored to supported lipid membranes by one or several porphyrins has been examined.<sup>8</sup> The porphyrin has been shown to be a multifunctional unit capable of operating as energy-donor and -acceptor, as an excited state electron donor and as a coordination site. Sequential energy- and electron-transfer has been demonstrated, starting from an excited state fluorescein in the water-phase the excitation energy is transferred to the porphyrin inside the membrane, where a benzoquinone transiently oxidizes the porphyrin.<sup>5</sup> Moreover, ligand specific coordination to both single and dimeric porphyrin constructs in the membrane has been demonstrated.<sup>9</sup>

**Keywords:** DNA base analogs, fluorescence, FRET, porphyrins, DNA, nanotechnology, lipid membrane.

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## Sergey Paramonov

*Crown ether annelated benzo- and naphthopyrans: synthesis, photochromism, and coordination ability towards metal cations and amino acids*

Mendeleev University of Moscow / University of Marseille

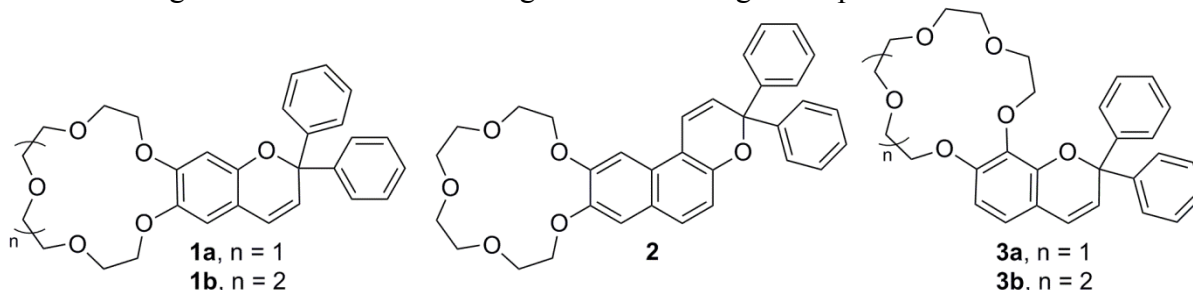
PhD Thesis: 2010

Supervisors: Prof., Dr.Sc. Olga Fedorova and Dr. Vladimir Lokshin

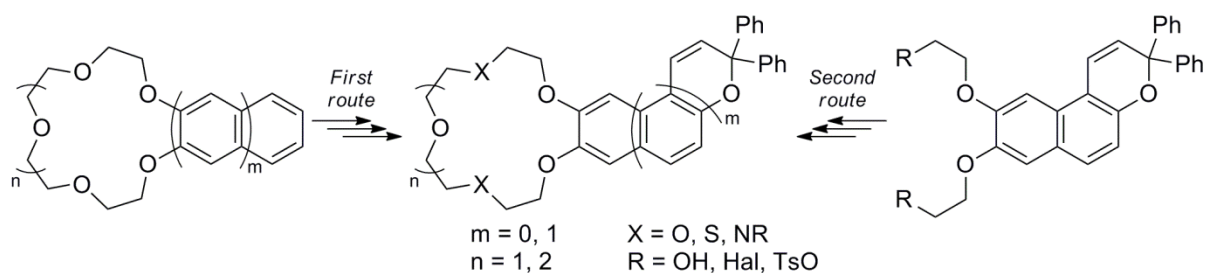
Incorporation of photochromic fragments into a molecule enables photo-control of its characteristics. This approach expands the possibilities of practical use of already known materials. The most well-known and widely used photochromes are spiropyrans, spirooxazines, and chromenes. The examples of photo-control of viscosity and size of polymer materials as well as characteristics and catalytic activity of biological molecules containing photochromic moieties are reported in literature. Of interest is application of photochromes to the control both intramolecular (charge and energy transfer) and supramolecular (host-guest coordination and complex formation) processes. The development of the latter trend is of importance for creation of nano-scale molecular devices for information processing and storage; design of new drugs with photo-controlled pharmacological activity towards various diseases including cancer; and enhancement as well as elaboration of environmentally safe technologies used in many branches of modern industry.

This work is focused on benzo- and naphthopyrans annelated by crown ether fragments and chromenes containing positively charged heterocyclic moieties. We were aiming at developing synthetic approaches to these compounds as well as comprehensive study of their photochromic and binding properties by NMR, optical spectroscopy, and X-ray structural analysis.

The use of the crown ether fragment as an additional functional group in the structure of photochromic compounds allows design of systems, in which photochromism and complex formation significantly affect each other. This is the basis for creation of systems with the photo-controlled complex formation or, vice versa, photochromic systems, which spectral and kinetic properties considerably depend on the presence of the metal cations (or other complexing agents). In the structure of the majority of crown-containing naphthopyrans, known in the literature, no macrocyclic fragment is included into the chromophore systems of the photochrome, but bound to it via a bridge. Therefore, in this work, we chose chromenes **1-3** containing annelated crown ether fragments as the target compounds.

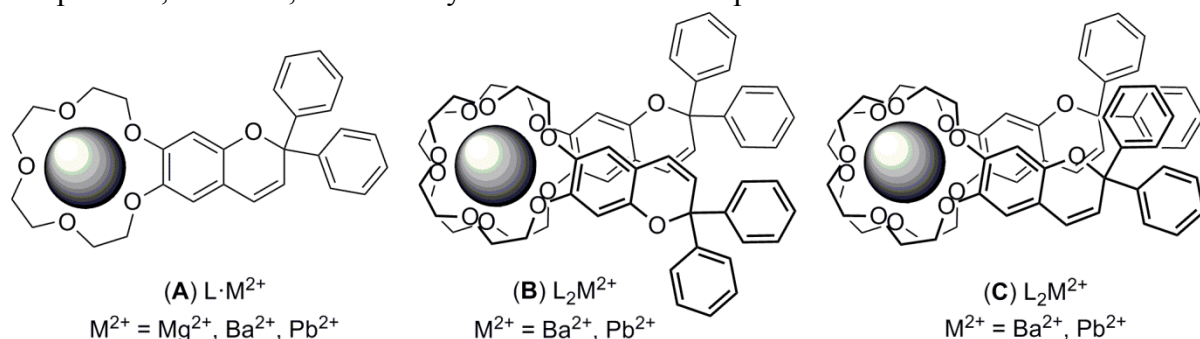


For their synthesis we developed two general strategies. The first, most obvious route consisted in the chromene fragment inclusion into the crown-containing aromatic substrate (benzo- or naphtho-15(18)-crown-5(6) ethers). The alternative route concluded, vice versa, in the crown ether fragment construction over the photochromic molecule.

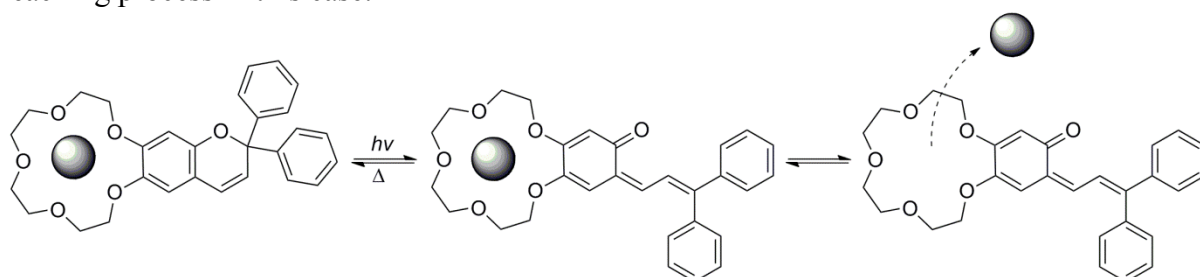


The first route appeared to be more efficient for the synthesis of mere oxo-crown ether chromenes. On the contrary, the second approach proved to be useful for the synthesis of chromenes containing crown ether fragments of different size and heteroatomic composition. In addition, we were able to apply the synthetic strategy to another important photochromic family, namely spirooxazines.

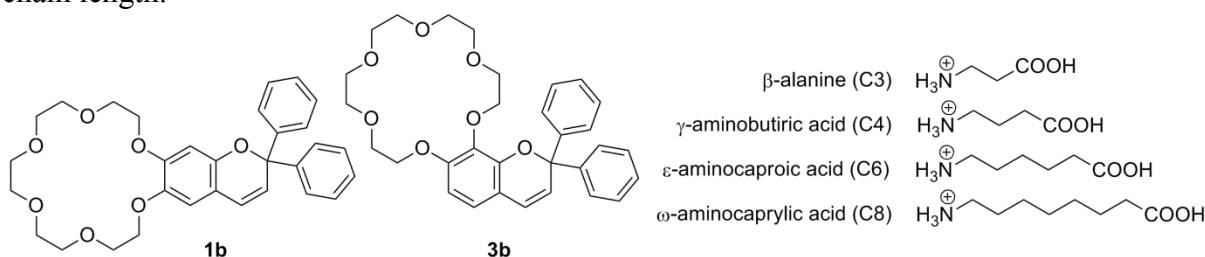
Further, we studied binding ability of chromenes **1a** and **3a** towards magnesium, barium and lead cations. Using UV-Vis and NMR spectroscopy, we determined the composition, structure, and stability constants of the complexes with metal cations.

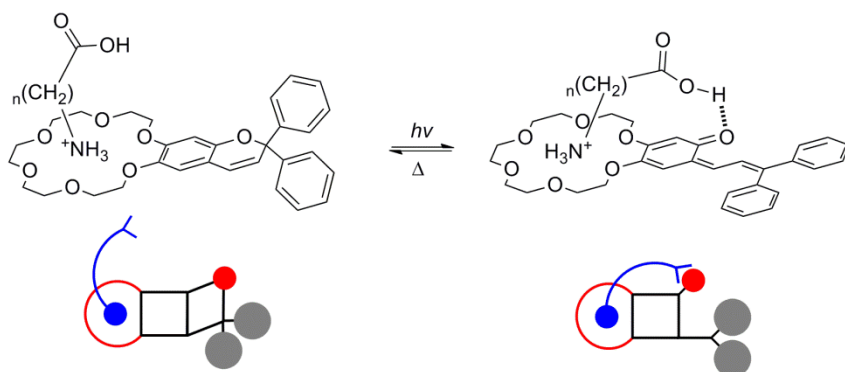


The investigations upon irradiation revealed strong mutual influence between the photochromic properties and complex formation. We found the stability constant of the complexes of the open forms is lower than those of the closed form; thus, irradiation leads to release of the cation. On the other hand, the thermal stability of the open forms in presence of the cations was found to be lower; consequently, we observe significant acceleration of the leaching process in this case.



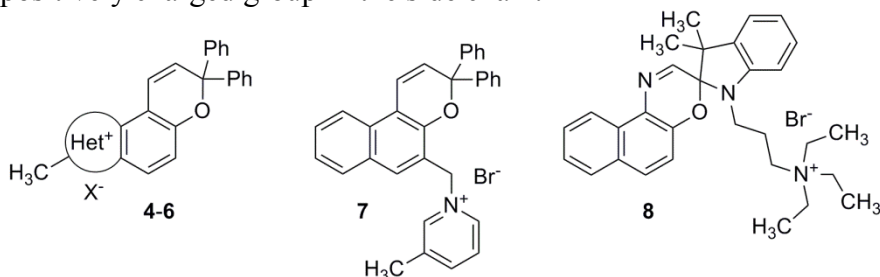
We investigated binding ability of chromenes **1b** and **3b** towards protonated aminoacids. We demonstrated that the acids can form either mono- or ditopic complexes with the open forms of the chromenes, the mode of complexation being dependent on the aliphatic chain length.





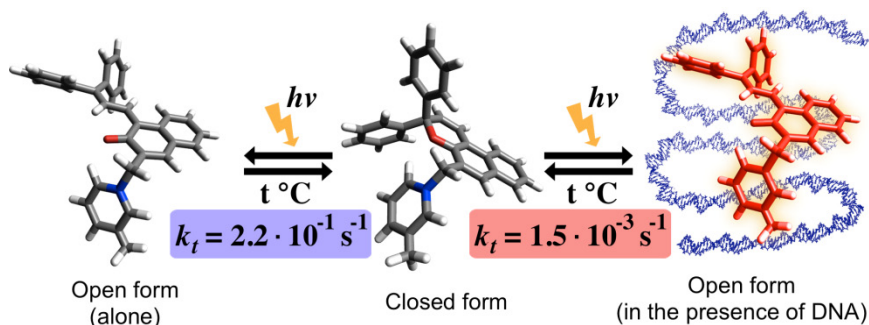
For example, we demonstrated that the mode of coordination of chromene **1b** with C5 amino acid may be switched using UV-irradiation as a trigger. The closed form of the chromene forms the monotopic 1:1 complexes with C5, whereas the photoinduced species forms the ditopic 1:1 complexes.

Another target of the work was the preparation of compounds able to participate in the photo-controlled DNA intercalation. In this case, the key requirement is the presence of positive charge in the structure. Therefore, we suggested several quaternary salts of heterocyclic chromenes **4-6** as well as chromene **7** and spirronaphthoxazine **8**, possessing positively charged group in the side chain.



Owing to their ability to transform upon irradiation into planar colored forms, photochromic benzo- and naphthopyrans may be used for reversible photo-control of DNA intercalation. In the initial state, these compounds are non-planar, as a result of the presence of two phenyl groups in the pyran ring. One may expect that before irradiation, due to spatial hindrance, no noticeable interaction with DNA will occur. Upon irradiation, the structure of the photochromes is substantially changed, it becomes planar, and as a consequence the probability that the open form gets inserted between the DNA base pairs increases. Thus, this property of the photochromes may be used to photo-control the intercalation process.

Further investigations revealed that only compound **7** can be successfully used for experiments with DNA. As expected, the initial form of the compound does not interact with DNA. Upon irradiation we observed significant stabilization of the open form of **7**. The observed effects were attributed to the intercalation of the open forms into DNA molecules.





## Małgorzata Insińska-Rak

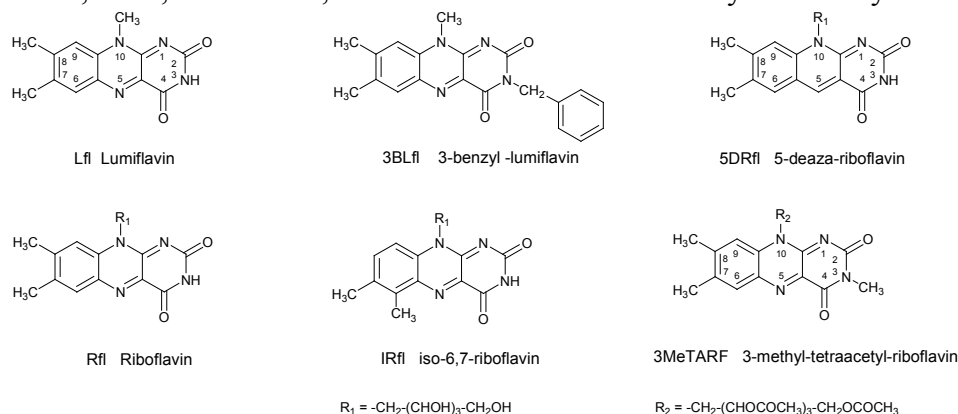
### *Riboflavine derivatives as singlet oxygen sensitizers*

A. Mickiewicz University, Poznan

PhD thesis: 2010

Research Advisor: Marek Sikorski

Flavins are compounds of considerable interest due to their biological function. Since it has been found that they are involved in numerous biological processes, they became an object of very intensive studies. The best known representatives of this group of compounds are riboflavin (vitamin B<sub>2</sub>), flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). The last two compounds, present in enzymes and photoreceptors, are known as the factors involved in metabolic processes occurring in living cells [1]. Riboflavin is known to undergo photoreactions with nucleic acids and to sensitize the destruction of tumour cells and intra- and extra-cellular HIV particles. These compounds play a catalytic role in processes such as pesticides oxidation and reactions with phenol or toluene derivatives [2,3]. There were also revealed their active part in pathogene destruction or inactivation of many viruses and bacteria [4]. Some research points out antitumor activity of riboflavin derivatives and their potential role in therapy of many other diseases [5]. Flavins structure contains isoalloxazinic system, which is responsible for their activity in diverse redox transformations. Therefore thorough investigation of spectral and photophysical properties and electronic structure of isoalloxazinic system seems to be crucial for explaining flavins reactivity and consequently mechanisms of flavin reactions in nature [6]. Presented dissertation is focused on the spectral, photophysical and photochemical properties of flavine analogues – 3-benzyl-lumiflavin, iso-6,7-riboflavin, 5-deaza-riboflavin and 3-methyl-tetraacetyl-riboflavin (**Fig. 1**).



**Figure 1.** Structures of studied riboflavine derivatives

Considering the fact that riboflavin is known as a good photosensitizer in the singlet oxygen formation reaction, a special regard was given to the role of investigated compounds in this process. However, deep insight into the complex processes in triplet excited states, demands thorough investigation of flavin photophysical and photochemical reactions. These requirements have been fulfilled by preparing the spectral and photophysical characteristics as measurements of absorption and emission spectra, excited state lifetime, determination of fluorescence quantum yield and contribution of radiative and non-radiative processes to excited states deactivation. There are also discussed the properties of some derivatives modified in position 3 of the isoalloxazine ring by an aryl substituent – 3-benzyl analogue – in comparison with derivatives modified by an alkyl substituent, namely 3-methyl and 3-ethyl

derivatives (known from previous study [7,8]). Some processes occurring in ground and excited singlet and triplet states of investigated analogues in solution were discussed in comparison with theoretical calculations obtained with using *Time-Dependent Density Functional Theory* (TD-DFT) and results of the transient absorption measurements. Additionally, there have been performed some spectral measurements for the studied derivatives in polycrystalline form, which enabled to observe influence of intermolecular interactions in a crystal system on spectral properties. Moreover some important research has been done to investigate the photochemical reactions of the studied compounds in methanolic solution.

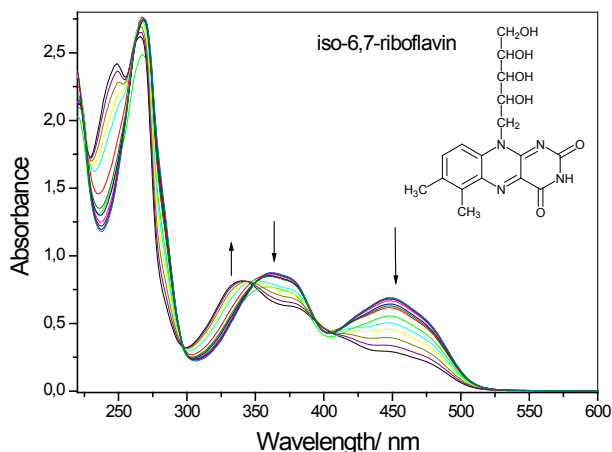
**Results:** Absorption spectra of the studied compounds consists of two intensive bands in short wavelength range and two relatively intensive bands in long wavelength range with maxima at about 360 nm ( $27.8 \times 10^3 \text{ cm}^{-1}$ ) and 450 nm ( $22.2 \times 10^3 \text{ cm}^{-1}$ ), which is characteristic for flavins. The studied derivatives fluoresce in room temperature and their emission spectra have one band with maximum at about 530 nm ( $18 \times 10^3 \text{ cm}^{-1}$ ) also characteristic for flavins. Fluorescence spectra were measured in methanol, acetonitrile and water. Fluorescence decay is characterized by monoexponential function.

The selection of riboflavin derivatives chosen for the study among other thing served to follow an influence of substituents on the spectral and photophysical properties of isoalloxazine system. Comparison of absorption and emission spectra of the lumiflavin derivatives with substituents in position N(3) of isoalloxazine system (3-methyl-lumiflavin, 3-ethyl-lumiflavin, 3-benzyl-lumiflavin) with lumiflavin spectrum shows that absorptive and emissive properties are not significantly influenced neither by the presence of substituent nor its size or type (alkyl, aryl). Their photophysical properties also remain unchanged by the substituents used in the study. Spectrum parameters in the case of 3MeTARF remain unchanged in comparison with riboflavin.

On the basis of *Time-Dependent Density Functional Theory* energies for the lowest electronic  $S_0 \rightarrow S_i$  transitions, electronic structure of triplet states, molecular orbital characters of  $S_0 \rightarrow T_i$  and symmetry of triplet excited states  $T_i$  were calculated. The investigations indicate that the lowest energy transitions have mainly  $\pi, \pi^*$  character, which are accompanied by  $n, \pi^*$  transitions of lower intensity. The obtained results of calculations reveal relatively good agreement with experimental results. Such closely located  $\pi, \pi^*$  and  $n, \pi^*$  states with  $\pi, \pi^*$  as the lowest transitions are characteristic for isoalloxazines, which allows to interpret some of isoalloxazine's properties on the basis of mutual interactions of singlet states of different character. Furthermore, some calculations related to triplet states were performed, which were compared to the experimental results obtained in the flash photolysis measurements.

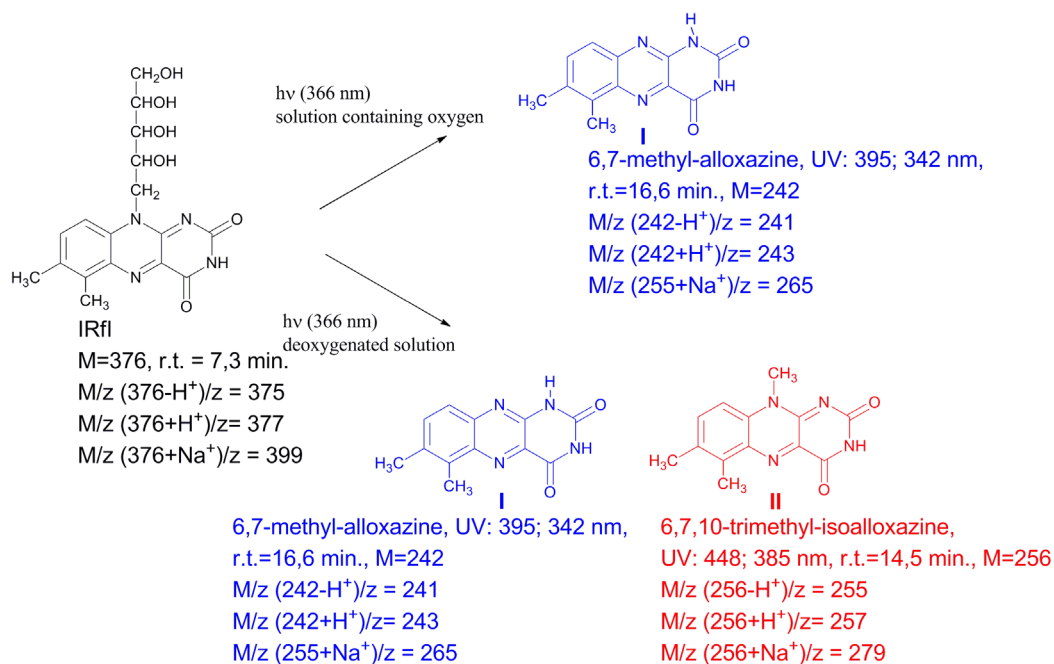
Diffuse reflectance measurements obtained for samples of 5DRfl and 3BLfl in polycrystalline form showed that bands in absorption spectra are shifted towards red in comparison to respective spectral bands in methanolic solution. Also maxima of emission spectra are shifted towards longer wavelengths for samples in polycrystalline form. Changes observed in the spectral and photophysical features reflect intermolecular interactions in the crystal system. Moreover, for 5DRfl a delayed fluorescence band was observed. In emission spectrum of iso-6,7-riboflavin there is an additional band in the short wavelength range that was attributed to 6,7-dimethylalloxazine formed in photoinduced degradation of iso-6,7-riboflavin in polycrystals under the experiment conditions. In the case of 3MeTARF only ordinary emission spectrum was observed. The lack of additional alloxazinic band (observed for riboflavin and iso-6,7-derivative) may be another confirmation of higher photostability of that molecule in polycrystalline form as well as in solution.

The studied compounds are quite susceptible to light-induced degradation (**Fig. 2**). In methanolic solutions the values of reaction quantum yields are of order  $\phi \sim 10^{-3} - 10^{-4} \text{ mol einst.}^{-1}$ . The main products of photolysis are respective alloxazine and isoalloxazine derivatives, which are also observed in the case of riboflavin (lumichrome and lumiflavin as the photoproducts) [9-12]. Degradation of the molecule occurs mostly within ribityl chain. Photolysis quantum yield in anaerobic conditions is higher than the analogous process in the presence of oxygen (in deoxygenated methanolic solutions  $\phi \sim 10^{-3} \text{ mol einst.}^{-1}$ ). The results led us to conclude that the triplet excited state was involved in the process.



**Figure 2.** Changes in absorption spectrum of IRfl in methanol, occurring in irradiation ( $\lambda_{irr} = 366 \text{ nm}$ )

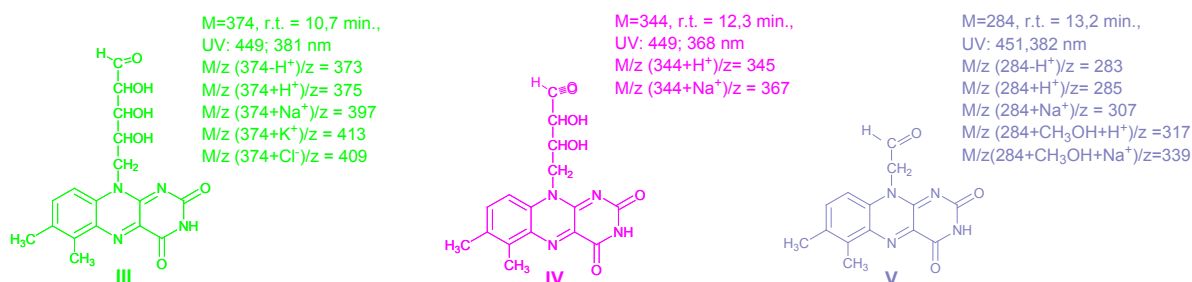
The quantum yield values of photochemical decay of the studied compounds (except 5DRfl) are lower than respective values obtained for riboflavin. In the case of 3BLfl irradiation conditions did not influence the quantum yield value, which in both anaerobic and aerobic conditions was  $\phi = 2.2 \times 10^{-4} \text{ mol einst.}^{-1}$ . On the other hand, different photoproduct distribution was obtained under oxygen conditions (**Fig. 3**). Irradiation experiment with 5DRfl and IRfl in the presence of oxygen gave rise to the alloxazine derivative. The presence of oxygen in photolysis cause that some reactions that involved triplet state are suppressed and reactive individual remains mostly flavin excited to singlet state, which probably leads directly to respective alloxazinic derivative. Under anaerobic conditions, formation of both isoalloxazine and alloxazine was found (**Fig. 4**). The mechanism of these reactions involves



**Figure 3.** Main photoproducts forming after irradiation of IRfl in methanol. Different photoproduct distribution depending on irradiation conditions

triplet state. Additional photoproducts were identified from the reaction mixture for two of the studied riboflavin analogues, namely iso-6,7-riboflavin and 5-deaza-riboflavin by means of mass spectrometry, HPLC and spectrophotometric methods.

The molecules of 3MeTARF are more photochemically stable than riboflavin itself. The value of quantum yield of its photolysis is at least two orders of magnitude lower than for the other studied derivatives. That higher photochemical resistance makes it possible to extend application of the compound as a model system in some riboflavin investigations. Figures 2, 3 and 4 represent results of the experiments for iso-6,7-riboflavin.



**Figure 4.** Suggested structures of additional photoproducts of irradiation of IRfl in methanol

It was shown that the molecules of the studied compounds in singlet excited states undergo intersystem crossing and populate triplet states very efficiently [13]. In this dissertation attention was focused on possible interaction between molecules of studied compounds with oxygen with special regard on singlet oxygen formation in photosensitized reaction. In order to evaluate these interactions some photophysical parameters, such as lifetime of triplet state, quantum yield of singlet oxygen formation and lifetime of formed singlet oxygen in methanol were determined. The value of singlet oxygen lifetime in methanol obtained in the experiment (10 $\mu$ s) is the same as literature data and additionally confirms the presence of the individual in the studied solutions during the experiment. The values of triplet state lifetime of studied compounds are in the microsecond time range, except for 3BLfl which is 34.9  $\mu$ s. Special interest should be given to the fact that studied derivatives sensitized singlet oxygen formation reaction with relatively high quantum yield. The values of quantum yield for these reactions are within the range (0.3-0.7) for the studied derivatives and are close to the value obtained for riboflavin (0.51).

**Conclusions:** Accurate knowledge in the spectroscopic aspects of riboflavin derivatives with substituted N(3) position of isoalloxazine core (3MeTARF, 3BLfl) allows to use them as a model system in the study of riboflavin, due to limited possibility of hydrogen bond formation. Absorption parameters of 3MeTARF in methanol remain unchanged in comparison with respective data for riboflavin. Moreover acetyl groups in ribityl chain make the molecule less polar (what enhances its lipophilicity and, in consequence facilitating its transmembrane transport) in relation to riboflavin and increase its photostability, which allows to extend its application as a good model object in a potential riboflavin investigations. On the other hand, in a molecule of 5-deazariboflavin carbon atom instead of nitrogen atom in the position (5) of isoalloxazine system cause significant changes of absorption and emission parameters. Since nitrogen atom in position N(5) of isoalloxazines is the position of considerable reactivity of a molecule, that structural changes makes 5-deaza derivative an attractive riboflavin substitute in a model study. There was relatively good agreement between the calculated data and the experimental results.

Photochemical investigations not only confirm a triplet state population, but also provide information that might be important for optimization of production respective products with

using flavin in photochemical reactions. Knowledge of photolytic processes concerning 5-deaza-riboflavin and iso-6,7-riboflavin with their structural differences in relation to riboflavin also enhance their potential application in a model study.

The obtained results suggest that the studied derivatives are good sensitizers of singlet oxygen formation in photosensitized reactions. They may have diverse applications which demand strong oxygenating individual such as singlet oxygen. Among all of them, photodynamic therapy is worth to mention. The results of presented research may also contribute to farther investigation and prospecting for sensitizers among riboflavin derivatives. From application point of view, the attractiveness of flavin derivatives enhances the fact that riboflavin as well as the products of its metabolic processes and photoreactions are nontoxic.

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## **Birger Hauchecorne**

*Development of an FTIR in situ reactor for real time study of surface reactions in photocatalysis*

**Universiteit Antwerpen**

**PhD thesis: 2011**

**Research Advisor: Prof. Silvia Lenaerts**

For many years, photocatalysis has been proposed as one of the promising techniques to abate environmental pollutants. To improve the catalytic efficiency, it is vital to know the reaction mechanisms of the photocatalytic degradation. Different methods are described in literature to study these mechanisms at the gaseous phase/photocatalyst interface with Fourier transform infrared (FTIR) spectroscopy as a commonly used method. The reactors described in literature and/or available on the market use external UV lamps which makes them prone to damage because of the need of additional, commonly quartz, windows. Not to forget the additional risk of the external UV light for the operators. Moreover, the currently available reactors are limited in their use for elucidating the different reaction mechanisms, because it

is not possible to look at the surface at the moment the reactions take place. Generally, the catalyst can only be investigated after the reactions have occurred, or it is only possible to look at the changes in the gas phase concentrations while the reactions are taking place. It is thus a major challenge to develop a reactor which makes it possible to detect changes on the catalyst surface at the moment the reactions are happening.

In this work, a new reactor is developed that will make it possible to study the catalytic surface at the moment the reactions occur, by means of transmission-absorption FTIR spectroscopy. Moreover, by using UV LEDs, it was possible to install the UV light inside the reactor area, so that no harmful UV light can leave the reactor, inherently making it a safer method. The reactor itself is completely constructed in stainless steel (SS316). It was also opted to construct the reactor in a modular way, so that every part was interchangeable and could easily be replaced according to the needs of the researcher. A special screw cap is designed to hold the UV LEDs on a printed circuit board and to fit in every standard FTIR spectrometer.

The reactor was thus designed with the purpose to perform transmission-absorption experiments so that the catalyst can be examined while the reactions are taking place on its surface. For the transmission-absorption mode, however, it is necessary to make the photocatalyst IR transparent, so that actual information regarding the reaction mechanism can be obtained. It was found that an amount of 60 mg  $\text{TiO}_2$  gives an IR transparent and gas permeable disk which can be used for the intended research. The major advantage of these kinds of disks is the fact that they are self-supporting, which ensures that the information gathered is only due to the catalyst itself, not from some kind of supporting material. The  $\text{TiO}_2$  disks were made by following the standard KBr disk producing method. Because this involves grinding and putting pressure on the powder, it is necessary to ensure that the catalytic properties are unaltered by these processes. For this, the surface area, pore size distribution, pore volume and crystallinity were followed throughout these processes.

The validation of this newly developed reactor is done by investigating the photocatalytic reaction mechanism of nitric oxide (NO) and comparing these findings with those already described in literature. It was found that NO is oxidised in nitrogen dioxide ( $\text{NO}_2$ ) and nitric acid ( $\text{HNO}_3$ ), which is exactly what was already proven from earlier studies found in literature. From these results, it became clear that the newly developed FTIR in situ reactor allows real time study of photocatalytic reactions.

Furthermore, two different pollutants of which the photocatalytic degradation mechanism was not yet known, were investigated as well. Both ethylene and acetaldehyde were chosen for a more thorough elucidation of their photocatalytic reaction mechanism. For ethylene it was found that there is a net change in dipole moment of the ethylene molecule with respect to the normal coordinated, when it is brought in the neighbourhood of the catalyst. From this finding, an hypothesis was formulated on how the CC-bond from ethylene will break. It was found that the aforementioned interaction between the catalyst and the molecule, allows the excited electrons from the UV irradiated catalyst to occupy the lowest unoccupied molecular orbital (LUMO) of the ethylene molecule through a process known as backdonation. Following this hypothesis, it was found that the degradation occurs through the formation of two intermediates: formaldehyde and formic acid, for which formaldehyde is bound in two different ways (coordinatively and as a bidentate). The oxidising agent in this particular reaction mechanism was found to be a series of OH radicals that are formed by the illumination of the catalyst in the presence of the already abundantly adsorbed water molecules on the catalytic surface. Finally,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are found as end products, resulting in the complete mineralisation of the pollutant. There was, however, no need for additional water in order for the reactions to take place.

The second case study, concerning acetaldehyde, showed that upon adsorption on TiO<sub>2</sub>, acetaldehyde was initially converted in crotonaldehyde by an aldol condensation. It was also proven that the formed crotonaldehyde is photocatalytically oxidised to formate (monodentate and bidentate) and bidentate acetate species, coming from formaldehyde, formic acid and acetic acid respectively. The formed bidentate acetate modes were found to be converted into formate species, which eventually lead to the formation of CO<sub>2</sub> by further oxidising these formate moieties. It is noteworthy that the conjugated bases are in steady state equilibrium with their respective acids and that in the case of formaldehyde, the presence of dioxymethylene species also were noted. From these measurements, a new photocatalytic pathway for acetaldehyde was presented.

The newly developed FTIR in situ reactor has proven to be a very useful tool in elucidating the photocatalytic reaction mechanisms of certain pollutants. The reactor itself is therefore currently in the process of being patented: after an encouraging search report, it was chosen to file the patent as a UK provisional filing in January 2010. Because this filing was promising as well, the patent procedure was extended towards a PCT filing, i.e. worldwide, in January 2011.

## Marco Cipolloni

### *Light Modulation of Chemical and Physical Processes: Molecular Systems with Potential Applications in Optoelectronics and Microlithography*

Università di Perugia

PhD thesis: 2011

Research Advisors: Prof. Giovanna Favaro and Dr. Fausto Ortica

Designing new functional materials for optoelectronics represents a continuous challenge which involves various branches of science. The expertise of physicists, chemists and engineers contributes to develop systems targeted to a desired function and improve their performances. A comprehensive characterization of such materials opens a window to the development of novel innovative devices. An interdisciplinary common effort becomes the key of the success in materials science. The feedback process is always needed: actual results, even failures, represent the basis of future development.

The object of this thesis fits into this context: it concerns the photochemical and photophysical study of photoreactive organic molecules belonging to the families of photochromic diarylethenes (DAEs) and photosensitive diazonaphthoquinones (DNQs). These compounds, as a result of interaction with electromagnetic radiation, can undergo structural rearrangements that produce reversible (DAEs, Fig. 1) or irreversible (DNQs, Fig.2) changes of color. Their light stimulated processes may be exploited in many technological applications.

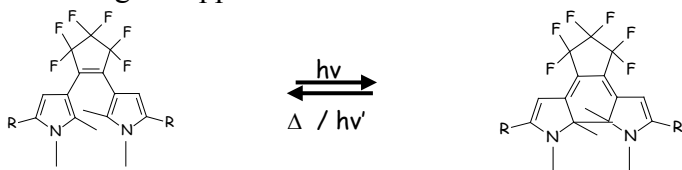


Fig. 1 The photochemistry of diarylethenes

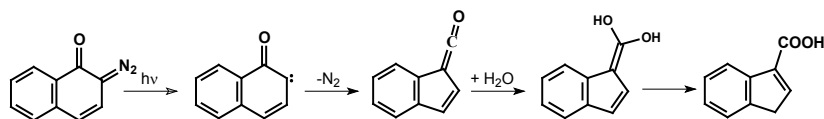


Fig. 2 The photochemistry of diazonaphthoquinones

As the photobehavior is determined by the competition of the different excited state relaxation pathways, it is important to know their contributions to the overall relaxation process. In this thesis reactivity was mainly studied by photostationary kinetic methods. Luminescence was investigated by steady state and time resolved fluorescence techniques. Additional information was provided by analyzing the effects of the temperature, solvent and irradiation wavelength on the photochemistry and photophysics. Searching for reaction intermediates and side products using time resolved laser flash photolysis and analyzing the reaction products by HPLC and NMR techniques yielded further insights.

To investigate the importance of structure modifications on the photochromic response, eight new photochromic diarylethenes, synthesized at the University of Marseille, were experimentally studied. They differ in the nature of the pentatomic cycle and aryl substituents, thiophene or benzothiophene, which are symmetrically or asymmetrically positioned in the diarylethenic structure (Fig. 3).

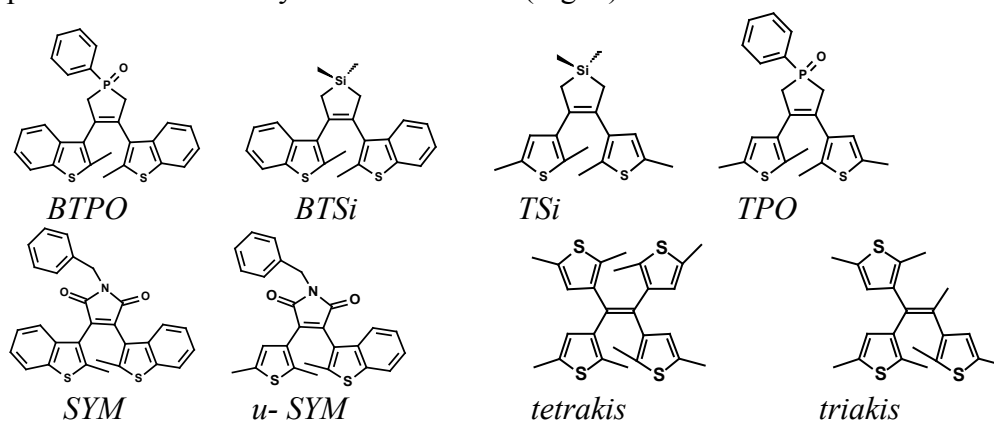


Fig. 3 Structures of the diarylethenes

Absorption and emission spectra and quantum yields of the cyclization ( $\Phi_{OC}$ ) and cycloreversion ( $\Phi_{CO}$ ) photoreactions, as well as of luminescence ( $\Phi_F$ ) were determined, highlighting significant differences in reversibility, photocolourability, temperature-dependence and fluorescence emission for the various compounds.

In terms of reversibility, the photochromic performance is especially promising when two thienyl substituents are symmetrically condensed with a phenyl, as it occurs in *BTPO*, *BTSi* and *SYM*, whereas in the absence of condensation (*TSi* and *TPO*) or with asymmetric substitution (*u-SYM* and *triakis*) photocolouration is accompanied by thermal and/or photochemical degradation.

Photocolourability depends on the photoreaction quantum yields ( $\Phi_{OC}$  and  $\Phi_{CO}$ ) and the molar absorption coefficient of the colored form ( $\epsilon$ ): the smaller  $\Phi_{CO}$  and the larger  $\epsilon$  and  $\Phi_{OC}$  are, the greater the maximum color intensity attainable. Consequently, at room temperature, the best colorability is provided by *BTSi* and *BTPO* for which  $\Phi_{OC}$  and  $\Phi_{CO}$  have close and rather great values ( $\sim 0.4$ ) and  $\epsilon \sim 8000 \text{ M}^{-1} \text{ cm}^{-1}$ . For *SYM*, despite  $\Phi_{OC}$  (0.14) is smaller than  $\Phi_{CO}$  (0.45), colorability is still reasonable due to a great  $\epsilon$  value ( $\sim 16000 \text{ M}^{-1} \text{ cm}^{-1}$ ) but it is quite small for *triakis* and *tetrakis* because of the little  $\epsilon$  value ( $\sim 3000 \text{ M}^{-1} \text{ cm}^{-1}$ ).



The temperature may significantly affect the photochemical quantum yields. Generally, the  $\Phi_{CO}$  promoted by visible light excitation decreases with decreasing the temperature, due to a barrier (of the order of a few  $\text{kJ mol}^{-1}$ ) to the ring opening reaction, which hampers the cycloreversion in a rigid matrix at 80 K (*BTSi*, *BTPO*, *SYM*, *triakis* and *tetrakis*). The photocyclization reaction is essentially barrierless and the  $\Phi_{OC}$  can even attain unitary value in a rigid matrix at 80 K. A “negative” temperature-dependence, that is an increase of  $\Phi_{OC}$  with decreasing the temperature, is attributed to an increased amount of the isomerizable (*anti-parallel*) DAE rotamer in the conformational equilibrium as the temperature decreases.

Fluorescence is as an additional switching signal that can increase the potential applications of photochromic diarylethenes. Some of the above molecules exhibited appreciable fluorescence emission ( $\Phi_F > 10^{-3}$ , lifetime in the nanosecond domain) in the colorless (*SYM*, *u-SYM*, *tetrakis*) and/or in the colored (*BTPO*, *BTSi*, *tetrakis*, *triakis*) forms. The luminescence occurring in the visible spectral region generally showed a large Stokes shift, which was attributed to emission from a TICT non-isomerizable singlet state.

To improve versatility in applications scientists are continuously searching for molecular structures where various signals can be triggered by different stimuli. The switching of several properties imparts new functionalities to photochromic systems and extend the possibility of their technological application. In this context, a multiswitchable acidichromic, photochromic and fluorescent *bis*diarylethene, synthesized in Marseille (*bis*DAE, Fig. 4), has been investigated from thermodynamic, photochemical and photophysical points of view.

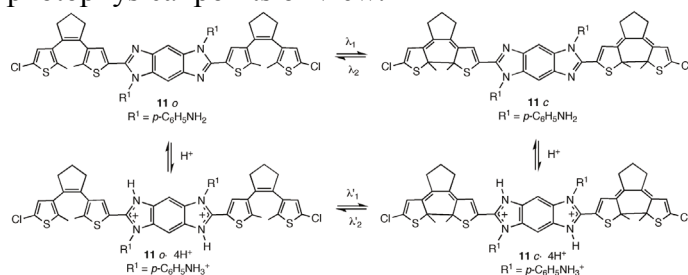
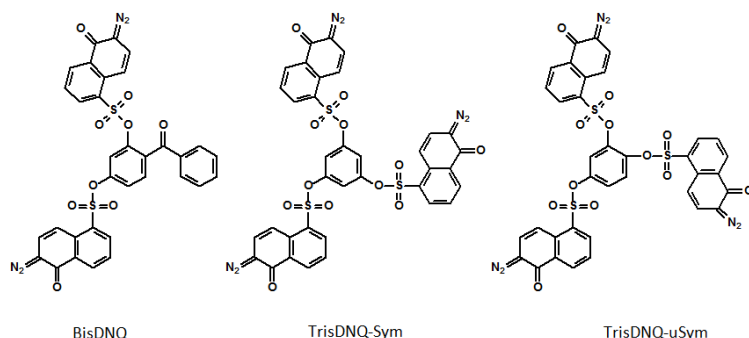


Fig. 4 Scheme of the acidichromism and photochromism of *bis*DAE

The *bis*DAE combines the diarylethene photochromic properties with the acidichromic and fluorescent properties of the benzobis(imidazole) central core. As schematically shown in Fig.4, such structure constitutes a multistate molecular switch, that can be independently triggered by light and pH. The solutions of this compound change color upon acid addition and/or UV-irradiation. Neutralization and/or visible-irradiation lead to bleaching. The color of both open and closed forms, as well as the color and intensity of the emission are modulated by the degree of protonation: with increasing the acidity, the lowest energy absorption band and the fluorescence band shift to the red. As the imidazole moiety becomes protonated the character of the emission changes from  $\pi, \pi^*$  to CT. These results mark out the *bis*DAE as a multi-state photochromic, acidichromic and fluorochromic compound. Such properties could be a stimulus for soft computing and fuzzy logic development.

Finally, some DNQs (Fig. 5), which are the photoactive components of the resists for integrated circuits, have been investigated to discover whether their photoreactions could be modulated by changing some experimental factors. The results show that by changing the solvent, excitation wavelength, temperature and concentration the course of the photoprocess changes, but is difficult to control. Intervention of thermal side processes, during or after irradiation, generates colored products that can negatively affect the performance in applications. However, it is noteworthy that the photochemistry can be performed throughout

a wide UV-vis spectral range, making it possible using a variety of laser sources for excitation, and that its effectiveness can be modulated by changing the excitation wavelength.



*Fig. 5 Structures of the DNQs studied*

It can be concluded that, as often it occurs in science, any research line leaves several open questions to be answered and rises new curiosities to be satisfied. However, from the results of this thesis and the huge number of data reported in the literature, it can be intuited that the synthesis of new compounds and the knowledge of their photobehaviors under different conditions may offer a variety of properties which can be tuned to the different requirements for applications.

## Damiano Genovese

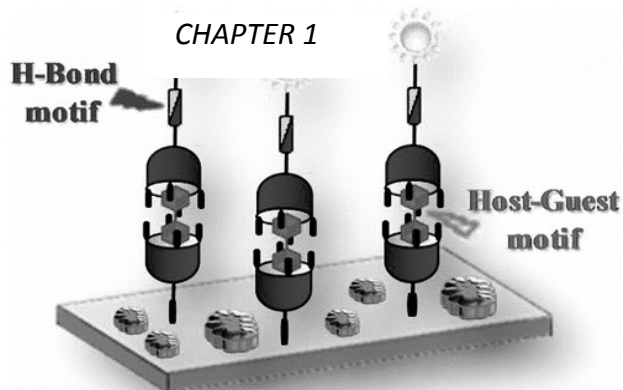
### *Supramolecular Approaches to Organized Luminescent Nanostructures for Sensing, Labeling and Imaging Applications*

Università di Bologna

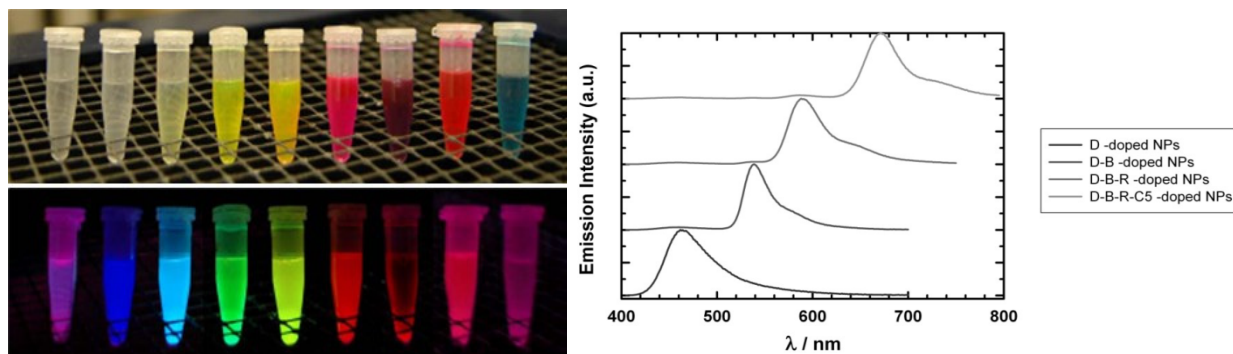
PhD thesis: 2011

Research Advisors: Prof. Luca Prodi, Dr. Marco Montalti, Dr. Nelsi Zaccheroni

The scientific method has taught us to break down the reality, factorizing it in small units. Be they real or not, they are easier to understand and manipulate, and actually constitute our access key to some comprehension of nature. The scientific method and the “factorization” of



reality in small units have brought us an enormous amount of knowledge, comprehension of natural phenomena, and ubiquitous concepts. After this phase in which scientists fragmented reality in its smallest bits, we are now called to build it back: we can use fragments —atoms and molecules with well-known properties— as elementary units for novel assemblies, featuring new emerging properties and functionalities.



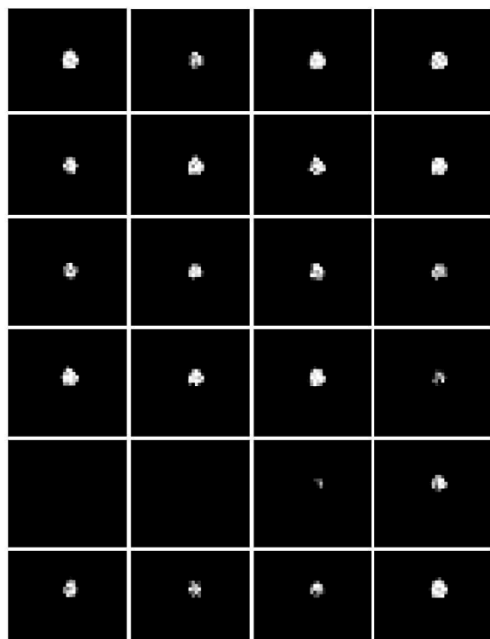
CHAPTER 3

The common thread that connects chapters and contents of this thesis is the will of investigating properties and behavior of such assemblies. Groups of objects display peculiar properties, which in some cases are very far from simply adding up respective components properties. This is truer, the smaller is inter-objects distance, i.e. the higher is their density: interactions between objects are in fact what makes their behavior change, and interactions are strongly dependent on the distance, as one can easily figure out in every field. “Confinement” is thus a key concept in many topics explored and here reported: it can be conceived as a spatial limitation, that yet gives origin to and boosts processes and phenomena otherwise hidden. Such phenomena eventually result in what we often refer to as “non-linear properties”, i.e. features that, being not linearly dependent on the density of objects, are responsible for the low predictability of the final behavior of the assembly.

Concepts such as confinement and non-linearity will be further explained and discussed, by means of experimental evidences, within the contents of this thesis. Almost every chapter will give a clue, with a different viewpoint, on such ubiquitous concepts.

Chapter 1 provides an insight on orthogonal non-covalent forces to build up a supramolecular structure on a surface. Such structure can thus be disrupted at different levels

## CHAPTER 5

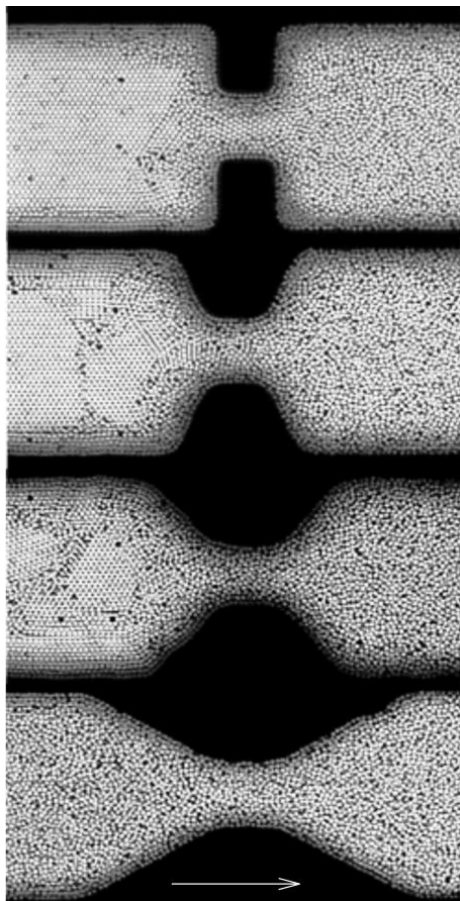


by means of suitable stimuli, and allows for different interchangeable functionalizations of a surface. Orthogonal forces allow for example different surface-wettability to be interchanged upon external triggers, or different functional groups to be placed or removed in a controlled fashion. Another surface study is discussed in chapter 2, in which a fluorescent sensor proves to work in a finely selective and sensitive way when embedded in a thin polymer film, coating a glass surface. The molecular structure of the sensor, bearing a cavitand linked to a fluorescent unit, ensures high selectivity towards short alkyl chain alcohols.

Supramolecular structures discussed in chapter 1 and 2 clear the way to nanotechnology in chapters 3 to 5. In these chapters we present systems where confinement of molecules (fluorophores) plays a major role, and discuss them under both theoretical and experimental points of view. The work focuses on processes of energy

transfer occurring between fluorophores within core-shell nanoparticles (NPs). Those are structures exhibiting nanometric size in all the three dimensions, where embedded molecules are confined in a “box” whose dimension approaches their own size. Dyes embedded in NPs will be shown to exhibit efficiencies of energy transfer close to unity, as required in

#### CHAPTER 7



demanding applications such as light harvesting for energy conversion, or in high throughput analytical assays. A model that allows simulations of global FRET (Forster Resonance Energy Transfer) events in NPs is presented in chapter 3, and quantitative indications and predictions are obtained, and used both in this and in the following chapters. Chapter 4 resumes the experimental work on dye-doped silica-core/surfactant-shell NPs (SCSSNPs). Properties of embedded dyes and of particles as ensembles are characterized and discussed. Inclusion of hydrophobic guests in particles' shell is proved. Exciting results of great applicative interest are drawn, such as a method of tuning emission wavelength by keeping constant the excitation one, and a way of overcoming self-quenching processes by setting up a competitive deactivation channel by means of FRET. We envisage applications of these materials as labels for multiplexing analysis, and in all fields requiring bright and tunable fluorescence signals coupled with biocompatibility and water solubility. Chapter 5 introduces a novel device based on adducts of dye-doped SCSSNPs and molecular photoswitches, with a main applicative goal in the context of superresolution techniques in fluorescence microscopy. This is a flourishing field that deserves room for targeted discussion, which the reader can find in Appendix to chapter

5. Chapter 6 focuses on a strongly applicative development of SCSSNPs. A method is proposed to prepare a library of functionalized surfactant Pluronic F127 polymers. Their micelles form template nanoreactors for dye and silica co-condensation, giving rise to a twofold “smart” nanomaterial, namely both (i) luminescent and (ii) surface-functionalized SCSSNPs. Both features can be easily tuned, virtually providing different photophysical parameters by changing kind and number of embedded dyes, and diverse surface properties, for example different (bio)receptors for any (bio)target, in the context of application of SCSSNPs as targeted labels.

Focus shifts, in chapter 7, from organization and interactions of molecular moieties in nanometrically confined particles, to the effect of confinement in an upper size scale. We move thus from nanometers to micrometers, and investigate the interplay between microparticles flowing in a microchannel. In this study, confinement effects are thus triggered by channel walls, affecting the properties of the strongly interacting ensemble of particles. The role of a constriction, in particular, is investigated, which affects at very long ranges both structure and dynamics of this dense colloidal paste. This fundamental study has interesting

applications in the field of polymer processing and extrusion, and in the field of oil recovery, whose importance increases as a result of the lack of easy accessible oil wells.

In conclusion, an excursus spanning from supramolecular structures, to nanoparticles, to a micrometric colloidal paste flowing in the millimeter length-scale, can be found in this thesis. Experimental methods used for all investigations converge in exploiting the phenomenon of fluorescence, useful to extrapolate information which is highly resolved in space and time, and which finely describes chemical environment and inter-dyes communication at sub-nanometric level. Theoretical models have also been developed and used to rationalize the highly efficient energy transfer events occurring in SCSSNPs; such nanoassemblies, in particular, revealed novel properties and unexpected behavior, which will possibly allow for use in many fields of application.

## CONFERENCE REPORTS

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### **RSC Photochemistry Group/Dublin Chemistry Photochemistry and Photochemical Techniques Meeting**

University College Dublin/Trinity College Dublin, Ireland, 16-18<sup>th</sup> May 2011

The RSC Photochemistry Group meeting was held in association with a Dublin Chemistry Graduate School workshop dealing with Photochemistry and Photochemical Techniques on the 16-18<sup>th</sup> May 2011. Building on the existing success of the Early Researchers one-day meeting organised bi-annually in the UK by the RSC Photochemistry Group, this event provided Photochemists from the UK, Ireland and across Europe with an opportunity to celebrate advances being made in the field and to establish new networks.

Increased security measures due to an unexpected visit by Queen Elizabeth II to Trinity College Dublin (TCD) on 17<sup>th</sup> May (the last British Monarch to visit Ireland was the Queen's grandfather King George V!) meant that the organising committee was forced to relocate the first part of the meeting. Fortunately the neighbouring institute University College Dublin (UCD) stepped in to save the day and provided excellent facilities at very short notice for the 100+ delegates who attended.

The meeting spanned over 3 days, starting at UCD on the Monday afternoon with two oral presentation sessions, followed with a wine reception and posters in the evening. A full day on Tuesday comprised 4 sessions of research presentations with another poster and wine reception, followed by the conference meal at Tenors Grill Room in Donnybrook. The meeting moved to TCD on Wednesday morning for the final two oral presentation sessions. In keeping with the spirit of the Early Researchers Meeting, the event was strongly focussed towards the participation of postgraduate and postdoctoral researchers, who made up the majority of contributions selected for oral presentation. In addition, the meeting featured keynote lectures from several invited speakers, who also provided a didactic background to their area of expertise. This approach proved popular with everyone present, with both new and experience researchers agreeing that they had discovered a lot and that there was plenty more to learn!

Prof. Thomas Gustavsson (Laboratoire Francis Perrin, CEA/Saclay) opened the meeting with a fascinating lecture on the use of ultrafast fluorescence spectroscopy and fluorescence upconversion to study relaxation processes in DNA and its constituents. On the second day Prof. Conor Long (Dublin City University) guided the audience through the use of quantum chemistry to study CO-loss by a series of "dark" states from homoleptic metal carbonyl complexes. Prof. Mike Towrie (Rutherford Appleton Laboratory) opened the afternoon session with an informative discussion on advances in ultrafast time-resolved vibrational (infrared and Raman) spectroscopic techniques and their application in fundamental solution phase photochemical research. The day was concluded by a public lecture by Dr Anita Jones (University of Edinburgh) who demonstrated that the fluorescence microscopy techniques (e.g. scanning confocal microscopy, two-photon excitation microscopy and fluorescence lifetime imaging) commonly used in Biology also have an important role to play in Physical Sciences research. This was followed by the Annual General Meeting of the RSC Republic of Ireland Local Section. On the final day, the meeting returned to TCD and Prof. Paul Raithby (University of Bath) closed the meeting with a

compelling insight into the use of “photocrystallography” to investigate reversible and irreversible photoactivated solid state processes.

Prizes for the “best oral presentation” and “best poster presentation” and runners-up in each category were awarded courtesy of sponsorship by Aldrich Materials. Elizabeth Baggaley (University of Sheffield) won “best oral presentation” for her talk “Time-Resolved Emission Imaging Microscopy: Autofluorescence-Free Imaging with Platinum (II) Dyes”. The runner-up was Oksana Shvydkiv (Dublin City University) who talked about “Microphotochemistry – Photochemistry in Microstructured and Continuous Flow Devices”. Martin Ward (University of Edinburgh) won the best poster prize, with Yilei Wu (Imperial College) taking the runner-up spot.

From the feedback, it seems that the first RSC Photochemistry Group/Dublin Chemistry meeting was a great success, with positive comments from participants about the mixed and diverse sessions, the programme, and the networking opportunities. The organising committee would like to thank the following sponsors for their generous support: RSC Republic of Ireland Local Section, Dublin Chemistry, RSC Photochemistry Group, Horiba Scientific, Aldrich Materials. Finally, we would like to thank everyone who came to the meeting for making it such a success and we look forward to seeing you all again in the future.





*Dr Rachel C. Evans*  
School of Chemistry, Trinity College Dublin

## **XXV<sup>th</sup> International Conference on Photochemistry (ICP 2011)**

Beijing, China, August 7-12, 2011

The XXV<sup>th</sup> edition of the International Conference on Photochemistry (ICP 2011), as part of the series of international photochemistry meetings, was held in Beijing (China) between August 7 and 12, 2011. After the 50 years of history of this series of conferences (the first one was celebrated in 1962 in Durham, USA), this has been the first time it was held in China. Prof. Chen-Ho Tung (TIPC-CAS, China) was the chairman of the Local Organizing Committee.

Around 360 scientists from 33 countries attended the conference, which contained three parallel sessions with 7 plenary and 51 invited lectures, 94 oral contributions and about 200 poster contributions that covered a wide range of research in the field using light to interrogate matter (Chemistry, Biology and Physics).

Among the topics of ICP11 were: excited state dynamics; primary photoreactions; photoinduced electron, proton, and energy transfers; photoprocesses in clusters and nanoparticles; photochromism; supramolecular and macromolecular photochemistry; photobiology; theoretical and mechanistic photochemistry; experimental techniques; as well as applied photochemistry and photophysics. Additionally, very interesting contributions in emerging topics (photovoltaic devices, liquid interfaces, nanophotonics, nanofabrication and



sensors) that are being developed during the last decade, were also presented and discussed during the conference.

ICP 2011 was inaugurated with an opening ceremony where the chairmen of the Local (Prof. Chen-Ho Tung) and International (Prof. Abderrazzak Douhal) Committee of the conference not only stated the objectives of the meeting, but highlighted the opportunity to discuss and create new partnerships between research groups that would enable further progress in this scientific field.

After the welcome session, the scientific part of the conference started with a plenary lecture delivered by Prof. Eric Vauthey (Switzerland), who showed how the ultrafast spectroscopy can give us valuable and unknown information about liquid interfaces by measuring the interfacial excited-state dynamics of selected molecular probes. Prof. Atsuhiko Osuka (Japan), in his plenary lecture showed how to improve applied photochemistry by optimizing design and synthesis of subporphyrin. Prof. Prashant V. Kamat (USA) focused his talk on new results on quantum dots photodynamics and the growing interest in



**Figure 1.** International Scientific Committee of ICP 2011 during the Opening Ceremony.

developing new systems aimed to create new, efficient solar cell prototypes. Using nature as an inspiration, Prof. Lei Jian (China) reviewed the advances in the fabrication of new biologically based smart multiscale interfacial materials. Following his talk, the presence of sense, drive and control is inherent in this type of materials and, thus the control of the proposed devices is improved. Prof. Norbert A. Hampp (Germany) in his lecture explained how two-photon absorption spectroscopy can be applied in ophthalmology to study the implantation of polymeric intraocular lenses (IOL) for drug release and refraction control. Prof. Abderrazzak Douhal (Spain) presented the current state of the art in molecular confinement. He reviewed studies of confined chromophores in chemical and biological nanocavities using time-resolved ensemble average and single molecule techniques. Another area of the applied photochemistry was considered by Prof. Soo Young Park (Korea), who discussed new strategies to develop and manipulate the performance of new photoluminescence materials with  $\pi$ -conjugated organic molecules of interesting nanophotonics, fluorescence- and ion sensing.

The invited and oral contributions were delivered during 3 parallel sessions. Each thematic session started with one or two invited lectures, to introduce the topic of the related session. The following oral contributions gave more developed research stories within the

framework of the topic. In this edition of ICP, the participation of young researchers and PhD students in the oral presentation was higher than in the previous ones. Personally, I think that this was a good idea, because it gave the opportunity to the young researchers to present, explain and discuss their advances in science.

The poster sessions (in the evening of two days), not only continued the scientific presentations, but also offered to the students a chance to interact with young and senior scientists and to participate in discussions on the different topics already addressed during the congress. Three poster awards have been delivered to the best presentations by PhD students and in this edition were assigned to: Keita Muraok (Hokkaido University), Liang Su from (University of Leuven) and Jaesung Yang (Yonsei University).

But, The ICP11 wasn't only about science; the organizing committee proposed several social activities that allowed the participants to enjoy the culture, food and architecture of one of the world's largest cities, Beijing, also known as "the capital of four dynasties". In these activities we enjoyed the visit of the Summer Palace and tried typical Chinese food during the banquet dinner, while having fruitful scientific discussions with fellow researchers.

The participation in this kind of high scientific quality meetings provides the possibility of discussing the advances made in the recent years, as well as giving the opportunity to create new collaborations and of course to learn about other cultures. For a PhD student, like me, attending this conference gave me the possibility to live a scientific and cultural experience which provided me new challenges.

Usually during and after attending a scientific meeting, there remains an open question: where are we going, and what are going to be the new advances in the field? This interesting and hard question is difficult to answer as nobody can predict the human heart's desire for developing science and technology. One way to know about the future is to wait for the new edition of the ICP (ICP 2013), to be held in Leuven (Belgium) and which will be organized by Professor Johan Hofkens, as chosen by the International Committee of ICP. So, see you there!

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## 21st Meeting of the Inter-American Photochemical Society

Mendoza, Argentina, May 17 – 20, 2011

This was the fourth meeting of the Inter-American Photochemical Society (I-APS) that took place in Latin-America. The first one in Iguazú dates back to 1996, the second was in 2001 in Ascochinga (Córdoba, Argentina) and the third was in 2006 in Bahía (Salvador, Brasil). This five years rhythmus permits to assess how much the Latin-American photochemical community grows and how much the subjects treated deepen and research lines get established. The meeting also naturally served to tighten or establish scientific ties between the Latin-American colleagues (especially the very young ones) and their North-American colleagues and some Europeans. The meeting was held in the Aconcagua Hotel and Convention Center, one of the several hotels that the nice City of Mendoza has to offer. Mendoza is a very vital City in the Province of the same name, very well known abroad for its excellent wines and also for its mountains, the highest in the Andes.

The scientific Committee was constituted by Pedro Aramendía (Argentina) Ana Moore (USA), Gonzalo Cosa (Canada), Mónica González, Valeria Kleiman (USA), Teresa Atvars (Brasil) and Elsa Abuin (Chile). The local organizing Committee was formed by Beatriz Barja, Mónica González, Carolina Lorente, María Julia Roberti, and Andrés Thomas (all five from Argentina).

The meeting was preceded by a Workshop treating specific photochemical aspects mostly related to the questions of solar energy conversion (see separate report).

All 31 lectures (each one took 40 min including discussion) were followed by lively discussions and comments. Tito Scaiano (Canada) open the lectures session speaking about “Plasmon transitions and their application in organic chemistry”, Fernando Sigoli (Brasil) spoke on “Rare earth doped luminescent materials”, Alexander Brolo (Canada) on “Plasmonic materials for biosensing”, Luisa De Cola (Germany) on “Luminescent soft and hard assemblies”, Guillermo Bazán (USA) on “Narrow band semiconductors for solar cell fabrication”, Alan Aspuru (USA) on “Combinatorial quantum chemistry for organic photovoltaics”, Claudio Borsarelli (Argentina) on “Photochemistry in macromolecular systems: from humic acids to proteins”, Richard Cogdell (Scotland) on “How purple photosynthetic bacteria harvest solar energy”, Gonzalo Cosa (Canada) on “Moduation of photophysics and photochemistry of polyelectrolytes via interactions with nanobeads and lipid vesicles”, Bruno Robert (France) on “Molecular basis of photoprotection in photosynthetic organisms”, James Mc Cusker (USA) on “Identifying reaction coordinates for ultrafast excited-state dynamics”, Michael Hoffmann (USA) spoke on “Artificial photosynthesis via the photoelectrochemical and photocatalytic reduction of CO<sub>2</sub> with the simultaneous production of H<sub>2</sub>”, Gustavo Argüello (Argentina) on “Laboratory studies of peroxy nitrates”, Daniel Mártire (Argentina) on “The employment of humic substances in photochemical experiments”, Chad Jafvert (USA) on “Sunlightmediated reactions involving C<sub>60</sub> and functionalized single-wall carbon nanotubes in aquatic environment”, Josef Michl (USA) on “Designed singlet fission as a possible tool in photovoltaics”, Dick Weiss (USA) on “What controls the fates of pyrenyl singlet states and benzylic triplet radical pairs in the melted and glassy states of poly(alkyl metacrylate)s?”, Alexis Aspee (Chile) on “Photo-induced free radicals for the study of antioxidants behavior in complex biological systems”, Sergio Bonesi (Argentina) spoke on “Application of photochemical reactions in organic syntheses”, Alicia Peñeñory gave a talk on “Photoinduced electron transfer chemistry”, Carlos Silva (Canada) on “The mechanism of efficient charge photogeneration in semicrystalline polymeric semiconductors”, Teresa Atvars (Brasil) on “Morphology of polymer blends in electroluminescent devices”, Ksenija Glusac (USA) on “Photochemical

and electrochemical behavior of flavin derivatives”, Victor Batista (USA) on “Oxomanganese complexes for natural and artificial photosynthesis”, German Günther (Chile) on “Sucrose monoesters and microheterogeneous systems”, Luis Otero (Argentina) on “Supramolecular dyes for Optoelectronics”, and Gerald Meyer (USA) on “Solar energy conversion with molecules”.



Many of the lectures were excellent and worth mentioning, but the lecture by Dwayne Miller (Canada and Germany) “Making the molecular movie: first frames...coming features”, deserves a very special comment because it was fascinating the way he brought the audience to a high emotional state by describing his (and his group) 14 years long efforts to develop the now ready “ultrabright electron source capable of atomically resolve structural dynamics with 100 femtosecond time resolution”. He said: “we have the technique, now we need biological samples”. So, let’s go work with him.

Two special lectures are always a highlight in the I-APS meetings. One is the Cilento award for a young scientist. The awardee this year was Laura Dántola from La Plata, Argentina, who gave a talk on “Production and quenching of reactive oxygen species by pterin derivatives”. The other special lecture was given by Kevin Stampelcoskie from Ottawa, Canada, the awardee of the Closs Prize. His lecture was titled “Using the plasmon absorption of silver nanoparticles to a maximum”. Both awardees made an excellent presentation and certainly deserved the respective prize.

Three very lively poster sessions allowed the younger colleagues and students (as well as the not-so young) to present and discuss their results in a more than friendly atmosphere. A total of 114 posters were presented during the three sessions.

It was nice to see the participation of colleagues and young students from Colombia, Puerto Rico, and Mexico, in addition to the larger number of colleagues from the USA, Canada, Chile, Brasil, and Argentina.

Besides the support from the Argentinean National Research Council (CONICET) and the Research Corporation for Science Advancement (USA), several firms, producing optical and electronic instruments, such as Horiba-Jovin Yvon, Edinburgh Instruments, CVI, Renishaw, Laseroptics, and Buckman, sponsored the meeting, exhibited their products, and some of them offered lectures about some of their equipment.

We all enjoyed the wonderful welcome reception on Tuesday evening in a winery. The weather could not be better, the food and wine were exceptionally good and the atmosphere was very friendly. On Friday night we enjoyed also the dinner with excellent meat (what else in Argentina?), although the traditional dancing was missing because there was not enough space for it.

The organizers did a wonderful job and should be congratulated for their planning, engagement and dedication.

As proposed by Jean Cadet, Editor-in-Chief of *Photochemistry and Photobiology (P&P)*, who also attended the Meeting, a Symposium-in-Print will be published as special issue of the Journal, with lectures presented at the Meeting. Gonzalo Cosa and Andrés Thomas are the guest editors of the issue.

I would like to mention that the ELAFOT XI, that is the 11th meeting of the Latin-American photochemists, will be in Córdoba in October 2012.

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## **21st I-APS Pre-Symposium Workshop**

Mendoza, Argentina, May 16th -17th

Several attendees of the 21st Conference of the Inter-American Photochemical Society arrived in Mendoza, Argentina, early to participate in a pre-conference workshop organized by Ana Moore (Arizona State University), Gonzalo Cosa (McGill University) and Valeria Kleiman (University of Florida). Reflecting many of the topics explored during the conference, but focusing on solar energy conversion and artificial photosynthesis, the workshop comprised contributions from throughout the Americas, from Canada to Chile and Argentina, and facilitated an informal atmosphere allowing for lively discussion of the presented subjects. The workshop offered an opportunity to discuss several techniques used in the photochemical sciences and was the perfect setting for the participation of young researchers who are at the beginning of their careers like Mike Hamburger from the US, Ernesto Mariño-Ochoa from México and Rodrigo Palacios from Argentina. The presentations were organized into three sessions covering energy and electron transfer in natural and artificial systems, experimental and theoretical methodologies, and novel materials. The workshop culminated in a round table discussion regarding the progress of research in Chemistry throughout and between North and South America through education and collaboration.

The first collection of speakers addressed the topic of energy and electron transfer in natural and artificial systems. This initial session, chaired by Ana Moore, saw contributions from Ksenija Glusac of Bowling Green State University, Gabriela Lagorio of Universidad de Buenos Aires, Mauricio da Silva Baptista of Universidade de São Paulo and Andrés Thomas of Universidad Nacional de La Plata. Also during this session, Luis Baraldo of Universidad

de Buenos Aires presented work on cyanide-bridged Ru(bpyridal)<sub>3</sub> complexes and their incorporation into dye sensitized solar cells. Mike Hamburger of Appalachian State University discussed the use of cobalt-based catalysts for the generation of hydrogen, and Rodrigo Palacios of Universidad Nacional de Río Cuarto described techniques for exploring electron injection into TiO<sub>2</sub> at a single particle level.

Presided by Gonzalo Cosa, the second group of speakers encompassed the topic of experimental and theoretical methodologies and began with a presentation by Marcia Levitus of Arizona State University on spectroscopic techniques for probing photophysical properties with single molecule resolution. James McCusker of Michigan State University discussed the use of time resolved spectroscopy in studying charge transfer of metal complex-based chromophores during this session. Also presenting during this portion of the workshop were Valeria Kleiman of the University of Florida, Su Lin of Arizona State University, Nancy Levinger of Colorado State University, Alan Aspuru-Guzik of Harvard University, and Sebastián Fernández-Alberti of Universidad de Quilmes.

With Valeria Kleiman as chair, the final session covered novel materials and enjoyed contributions from Carolina Aliaga-Vidal of Universidad de Santiago de Chile on manipulating the fluorescent properties of gold nanoparticles, Ernesto Mariño-Ochoa from Tecnológico de Monterrey covering axial modification and functionalization of (Si)-phthalocyanines, and Qyuen Nguyen of the University of California Santa Barbara discussing advances in plastic solar cells. The session concluded with an insightful presentation by Tom Moore of Arizona State on the pressing need for new energy paradigms especially relating to artificial photosynthesis.

Finally, the last session of the workshop consisted of a round table discussion on the promotion of research in Chemistry in Latin America, especially through joint educational and collaborative efforts with North America and Europe. The discussion began with perspectives and anecdotes from the panel, formed by Ana Moore, Silvia Braslavsky, Pedro Aramendía, and Teresa Atvars, later involving the greater audience in a rich discourse on the topic. Various aspects of the collaborations were considered, such as brain drain of Latinamerican scientists, establishment of new technologies in Latin- America, possibilities of funding of joint collaborations, etc. In all, the workshop of the 21st-I-APS Conference provided the participants with a broad sampling of the topics further explored during the invited talks and poster sessions of the 21st-I-APS conference that followed (see separate report) as well as the opportunity to discuss both the research and broader issues relating the field of the photochemical sciences in a smaller and more informal setting.

*Benjamin Sherman*  
Arizona State University

## INVITATIONS

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### CECP 2012

Bad Hofgastein, Austria, February 5 to 9, 2012



Dear Colleagues,

we are delighted to announce for the sixth time a conference on photochemistry in the Gastein Valley in Austria, February 5 to 9, 2012. After 1998, 2004, 2006, 2008, and 2010 where we met us in Bad Gastein and Bad Hofgastein, respectively, organized by Horst Kisch/Erlangen, Axel. Griesbeck/Cologne, and Stephan Landgraf/Graz we hopefully will come together again next spring. The local organizer is the Austrian section of EPA. The conference site is the Congress Centre of Bad Hofgastein (same as in 2006 to 2010) which is in fact an ideal location with a reasonable price.

The meeting is intended to bring researchers from central Europe together to exchange their experiences and results. Young scientists and coworkers are also requested to come. They will have to pay a low fee and a limited number of travel grants will be available on request. The conference is an open meeting for all aspects of photochemistry and also for all groups worldwide. Due to the excellent facilities we have booked for you, the conference can accept a maximum number of 120 participants. The poster space is also practically unlimited (about 100).

To register to the CECP 2012 we would like you to fill in the registration form that is available for download and return it to the local coordinator ([info@cecp.at](mailto:info@cecp.at)). Note: the deadline for oral contributions will be December 1, 2011. We have a strict evaluation procedure to ensure best quality of the meeting. So be sure to send your abstract(s) with your best results to this meeting.

At Bad Hofgastein we will have a variety of different accommodations available from hotels (3 or 4 stars at special rate) to private rooms. All of them are very near to the conference site in a range of 5 to 10 min on foot. You will get a buffet each evening (Su to We) so that you need only bed and breakfast. Sessions will be in the morning and in the evening. During the afternoon there will be enough time for physical activities, like downhill or cross-country skiing, walking, and a visit in the Alpen Therme Gastein (thermal bath and spa).

We are looking forward to see you next spring,

*Stephan Landgraf*

Local coordinator of CECP 2012, chairman of EPA Austria

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