



European Photochemistry Association

NEWSLETTER

December 2008

General information about the European Photochemistry Association

is available at:

www.photochemistry.eu

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MEMBERSHIP APPLICATION FORM

EDITORIAL

President's Letter

An important process aiming to take the European Photochemistry Association to new frontiers is under way. A crucial step towards this direction was to acquire appropriate statutes reflecting current practices which has now been completed and details can be found on page 8. The Executive Committee had proposed a revision of the statutes, which after being circulated amongst members, were approved by the EPA General Assembly held during the IUPAC Symposium on Photochemistry at Gothenburg last July (page 6). At this Symposium the two winners of the first EPA PhD Prize for the best thesis in the field of photochemistry, Maria Abrahamsson and Alexander Fürstenberg, received their prize certificates and presented their work (page 38). Also at the Symposium, a plenary lecture was sponsored by our journal *Photochemical & Photobiological Sciences* (Page 17); it was given by Professor Stefan Hell on the exciting topic of far field fluorescence nanoscopy.

The EPA has recently started a drive towards making photochemistry known to the wider public. David Phillips and I represented the Association at a Conference entitled "Opening up scientific research to learning communities" in Athens during September 2008 where the participants were experts in science education and communication. I hope to be able to give you more details about further activities in the forthcoming Newsletter.

The next important appointment for our community will be the International Conference on Photochemistry to be held at Toledo, Spain during July 2009 (page 48) which EPA members are warmly invited to attend. In order to benefit from reduced registration fees at the Toledo Conference, as well as the other member benefits - for example free access to the electronic version of *Photochemical & Photobiological Sciences* - don't forget to pay your membership fees (which remained unchanged) either to your Local Treasurer (for a list of local treasurers, visit the EPA website at <http://www.photochemistry.eu/join.php>) or to the General Treasurer Silvio Canonica. By doing this as soon as possible you can enjoy the member benefits through the year and you encourage the Executive Committee to undertake further actions promoting photochemistry.

Dimitra Markovitsi

MINUTES OF THE EPA GENERAL ASSEMBLY

Conference Centre, Gothenburg, Sweden, July 31st 2008

Agenda:

1. **Report on the action of the Executive Committee by D. Markovitsi (Chair)**
2. **Revision of the EPA statutes by D. Phillips (Past Chair)**
3. **Elections of the Executive Committee**

1. During the last General Assembly held at Cologne (July 30th, 2007), Chair David Phillips retired. Dimitra Markovitsi, already member of the Executive Committee (EC), was elected Chair. Two new members were elected to the EC: David Worrall and Werner Nau. The composition of the EC during the last year is given below. In addition to the collective action of the EC, each member had a specific task:

- **Silvio Canonica** (Switzerland) Treasurer
- **Nina Gritsan** (Russia) Membership
- **Helge Lemmetyinen** (Finland) Vice-Chair
- **Dimitra Markovitsi** (France) Chair
- **Sandra Monti** (Italy) PPS issues
- **Werner Nau** (Germany) Public relations
- **David Phillips** (UK) Past Chair
- **Eric Vauthey** (Switzerland) Web Manager
- **David Worrall** (UK) Newsletter Editor

The EC met three times as a whole; two partial meetings took also place in order to solve specific problems.

- a) Website: A new website was prepared. This contains also a member-only area.
- b) Newsletter: One electronic issue (December 2007) and one printed issue (June 2008) were produced. As the printing cost in the UK was too high the printing was carried out in Bologna with the help of Sandra Monti. However, this operation was too complicated. The EC should find a more viable solution by the end of the year. Many of the booklets sent by regular mail were returned because the address was not correct. Members are asked to check their contact details on the website and send their corrections to S. Canonica [silvio.canonica@eawag.ch].
- c) EPA PhD Prize: The Prize for the best thesis in the field of Photochemistry was awarded jointly to Maria Abrahamsson (University of Uppsala, Sweden) and Alexander Fürstenberg (University of Geneva, Switzerland). 23 nominations were received for theses defended in 2006/2007.
- d) Photochemical & Photobiological Sciences (PPS): This journal, created in 2002 is owned jointly by EPA and the European Society of Photobiology. It is published by The Royal Society of Chemistry with no page charge. It has the highest impact factor of all photochemical-biological journals: 2.208 in 2007. All EPA members have electronic access to PPS and are strongly encouraged to submit manuscripts. It is stressed that PPS publishes articles on the whole field of photochemistry, not only those in relation to photobiology. During the last year S. Monti and D. Markovitsi participated to two meetings of the PPS Ownership Board.
- e) Membership: On July 2007 EPA had about 800 members. Many of them were no longer active in the field and/or were not paying membership fees. Serious difficulties were encountered in countries where national treasurers did not collect membership fees. As EPA had to pay PPS subscription for all its members,

bankruptcy of EPA was expected to occur in a few years. In order to change this situation, special efforts were made by the Treasurer, assisted by N. Gritsan and E. Vauthey. Simplified payment via credit cards was introduced, the membership application form was sent directly to all members and the relation with the national treasurers was clarified. Thus, on July 2008 EPA had 552 members who had paid membership fees for this year. They originate from 31 different countries. It was proposed that the membership fee for 2009 remains 30 € for normal members and 15€ for PhD students.

- f) Financial report: The Auditors, Helmut Görner and René Williams, have approved the financial report presented by the Treasurer.
- g) Public relations: A flyer presenting EPA was produced by W. Nau with valuable help from Sarah Ruthven (RSC/PPS). The flyer was distributed in the package delivered to the participants of the IUPAC Symposium at Gothenburg.
- h) Conferences: EPA was associated with three conferences during the past year and there are plans for three others:
- Members paid reduced registration fees at the IUPAC Symposium.
 - The Austrian EPA Section organized the Central European Conference on Photochemistry (Hofgastein, February 2008)
 - A Photochemistry Summer School was organized under the auspices of EPA (The Netherlands, May 2008)
 - EPA will be represented by D. Markovitsi and D. Phillips at the Symposium “Opening up scientific research to learning communities” (Athens 2008)
 - EPA will participate to the organization of a Session on Solar Energy (D. Bassani) at the European Conference for Photobiology (September 2009, Poland)
 - The Italian Section will organize a Conference on the History of Photochemistry (July 2010)
- i) Promotion of awareness of photochemistry and its applications to the wider public: EPA was requested to act as a privileged holder to the European project **e-KNOWNET**, started in 2008 in the frame of the EU LIFELONG LEARNING PROGRAMME. The objective of this project is to facilitate the flow of knowledge between research laboratories and the general public. This pilot experience, whose output will be an electronic portal, will be focused on Photochemistry.

2. EPA was founded in 1970. A revision of its statutes was now deemed necessary in order to adapt to the evolution of the scientific and institutional contexts in Europe. The major changes in the statutes have been broadcast to members. The General Assembly approved the new statutes proposed by the Executive Committee.

3. The Executive Committee was proposed to continue for two more years in its present composition. It was re-elected unanimously.

THE STATUTES OF THE EUROPEAN PHOTOCHEMISTRY ASSOCIATION

TITLE I: Name, Headquarters, Permanence and Objects

ARTICLE 1

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

ARTICLE 2

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

TITLE II: Membership

ARTICLE 3

- (a) Membership of EPA is open to all scientists both from Europe and from countries outside Europe.
- (b) Membership is annual and is subject to a fee as assessed by the Executive Committee and approved by the General Council. Membership fees must be paid according to the rules established by the Executive Committee.
- (c) It is the responsibility of the members to provide and maintain correct contact details, including email addresses. Changes should be notified to the General Treasurer.

(d) EPA members of a given country may organize, by agreement with the Executive Committee, a national EPA section with a designated national representative who serves as a contact person.

(e) A national section may lose its status upon the decision of the Executive Committee.

ARTICLE 4

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

ARTICLE 5

Membership of EPA may be terminated at the request of the Executive Committee for just reason.

ARTICLE 6

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

ARTICLE 7

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

ARTICLE 8

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

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

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

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

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

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

ARTICLE 9

(a) The Executive Committee administers EPA.

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

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

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

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

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

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

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

TITLE IV: Finances

ARTICLE 10

- (a) EPA is a non-profit making organisation.
- (b) The income of the EPA shall consist of:
 - (1) Contributions of members as assessed by the General Council.
 - (2) Contributions from governmental bodies or national scientific societies representing member countries.
 - (3) Gifts, donations, and legacies.
 - (4) Grants, which may be accorded to it.
 - (5) Royalties from publications.
 - (6) Revenues from advertisements in publications.

ARTICLE 11

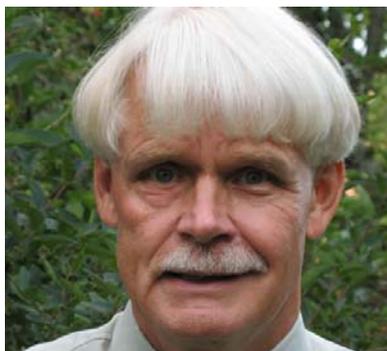
- (a) A national section may hold a account to which EPA members pay their dues and where other official revenues and expenses are recorded.
- (b) The person in a national EPA section responsible for the finances may be the national Local Treasurer. Local Treasurers are appointed by the Executive Committee.
- (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.

EPA EXECUTIVE COMMITTEE



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EPA PhD PRIZE

EPA prize for PhD Thesis on Photochemistry

The second EPA Prize will be attributed during the XXIIIrd IUPAC Symposium on Photochemistry which will be held in Ferrara, Italy in 2010. The awarded will present their work at the Symposium.

The Prize is 1000 Euros, plus travel costs to Ferrara (within the limit of 300 €) and one free year of EPA membership.

The candidate must:

- have defended his/her PhD Thesis in 2008/2009
- be nominated by an EPA member

Deadline for nominations: end of 2009

Please send nominations (electronically only) to Eric Vauthey
e-mail: eric.vauthey@chiphy.unige.ch

Nominations must include

- [1] a copy of the thesis
- [2] an abstract of thesis in English, no more than five pages
- [3] a list of publications arising from the thesis
- [4] a letter of support

THE HAMMOND MEDAL

The Hammond Medal: Description and Solicitation for its Endowment

A medal to honor the memory and contributions of George S. Hammond to the photosciences is being established, subject to reaching an adequate endowment. The Hammond Medal will be presented biennially to a scientist for lifelong achievement in any area of the photochemical sciences. The Awardee need not be a member of I-APS, and Porter Medalists and I-APS Award winners will be eligible; scientists from all parts of the world will be considered equally.

The Medal will be awarded biennially at an I-APS meeting in years that alternate with conferral of the Porter Medal. The Awardees will be requested to deliver a lecture as part of the presentation ceremony. The endowment will be administered in perpetuity by the Inter-American Photochemical Society (I-APS). Given the nature of the award, a minimum of US\$50K will be necessary to establish the award.

Donations to the endowment fund should be made payable to “I-APS Hammond Fund” and sent to the U. S. I-APS Treasurer:

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Ames, IA 50011-3111
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PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES

PLEASE NOTE: To enjoy continued access to PPS as part of your EPA membership, please ensure you provide your date of birth to the Treasurer, Silvio Canonica.

For the highest impact – publish in Photochemical & Photobiological Sciences

The official journal of the European Photochemistry Association, the European Society for Photobiology, the Asia and Oceania Society for Photobiology and the Korean Society of Photoscience.

Photochemical & Photobiological Sciences (PPS) publishes high quality research on all aspects of photochemistry and photobiology, including elemental photochemical and photophysical processes, the interaction of light with living systems, environmental photochemistry, environmental photobiology, the use of light as a reagent, how light affects health, the use of light as a diagnostic tool and for curative purposes and areas in which light is a cost-effective catalyst.

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 - Gene, Sequence and Cell Ontology terms linked to definitions and related articles
 - IUPAC Gold Book terms linked

Editors-in-chief:



Rex Tyrrell,
Bath, UK



Frans De Schryver,
Leuven, Belgium

Parameters affecting the chemical work output of a hybrid photoelectrochemical biofuel cell
Michael Hambourger, *et al.*, USA *Photochem. Photobiol. Sci.*, 2007, **6**, 431

Highly efficient supramolecular photocatalysts for CO₂ reduction using visible light
Shunsuke Sato, *et al.*, Japan *Photochem. Photobiol. Sci.*, 2007, **6**, 454

Conformational analysis of the blue-light sensing protein YtvA reveals a competitive interface for LOV-LOV dimerization and interdomain interactions
Valentina Buttani, *et al.*, Italy *Photochem. Photobiol. Sci.*, 2007, **6**, 41

Intracellular photodynamic therapy with photosensitizer-nanoparticle conjugates: cancer therapy using a Trojan horse
Martina E. Wieder, *et al.*, UK *Photochem. Photobiol. Sci.*, 2006, **5**, 727

Synthesis, structure and luminescence studies of heterometallic gold(I)-copper(I) and -silver(I) alkynyl clusters/aggregates
Sung-Kong Yip, *et al.*, China *Photochem. Photobiol. Sci.*, 2007, **6**, 365

Relation between intracellular location and photodynamic efficacy of 5-aminolevulinic acid-induced protoporphyrin IX *in vitro*. Comparison between human glioblastoma cells and other cancer cell lines
Reinhard Sailer, *et al.*, Germany *Photochem. Photobiol. Sci.*, 2007, **6**, 145



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PERSONAL NEWS

Symposium in honor of Dr. Esther Oliveros on the occasion of her 60th birthday

The date of Esther's 60th birthday coincided with her stay at Palermo, Italy, to participate in the SPEA5-meeting, and was celebrated in private with a typical Italian dinner. However, an event to meet with friends and colleagues was already organized, and on October 31, a Symposium in her honor took place at the *Centro de Capacitação e Pesquisa em Meio Ambiente* of the *Universidade de São Paulo* (CEPEMA-USP) at Cubatão, Brazil. The location was well chosen, because Esther is collaborating since many years with colleagues at the Laboratório de Simulação e Controle de Processos (LSCP-USP) on topics of process optimization and environmental techniques and was closely following the foundation of CEPEMA. The date of the Symposium in the eve of the IXth ELAFOT (Latinamerican Meeting on Photochemistry and Photobiology) made it possible for Esther's many Latinamerican friends and colleagues to celebrate with her.



The participants of the Symposium at the occasion of the 60th birthday of Esther Oliveros

Esther likes to create and to work in teams, and each of the 6 plenary lecturers of the Symposium represented one of past or present highly successful collaborations:

Claudio A. Oller di Nascimento, LSCP-USP, Brazil, (“Modeling of photochemical reactors”) highlighted the applications of artificial neural networks for the design of photochemical reactors.

Alberto L. Capparelli, Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA) and Universidad Nacional de La Plata, Argentina, (“Fotoquímica de derivados de la pterina en soluciones acuosas”) reviewed the success story of the last 15 years of pterin photochemistry.

Guillermo Orellana, Departamento de Química Orgánica I, Universidad Complutense de Madrid, Spain, (“Desinfección solar de agua mediante sensibilización con nuevos sistemas polímero-colorante y reactores CPC”) described new sensitizer systems for water disinfection using solar photochemistry.

Marie-Thérèse Maurette, Laboratoire IMRCP UMR 5623, Université Paul Sabatier, Toulouse, France, (Tratamiento de compuestos orgánicos volátiles (COV) por fotocatalisis y fotólisis UV-V (ultravioleta del vacio)”) compared the oxidative degradation of gaseous model pollutants by TiO₂-photocatalysis and VUV-photolysis.

Marta I. Litter, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica (CNEA) and Universidad Tecnológica Nacional (UTN), Buenos Aires, Argentina, (“Remoción de metales pesados en agua por fotocatalisis heterogénea. Mecanismos involucrados”) presented her work on the reduction of heavy metal ions by TiO₂-photocatalysis and its application in water treatment.

David G. Whitten, Center for Biomedical Engineering, University of New Mexico, Albuquerque, NM, USA, (“Oligo phenyleneethynylenes and poly phenyleneethynylenes: transitions from molecules to macromolecular properties and interfaces”) described cationic oligomers and polymers, their interaction with microorganisms and their potential for disinfection under irradiation.



The honoree and the plenary lecturers at the Symposium (from left: Guillermo Orellana, Marta I. Litter, David G. Whitten, Marie-Thérèse Maurette, Alberto L. Capparelli, Esther Oliveros, Claudio A. Oller do Nascimento)

Coffee breaks and lunch provided ample time to meet colleagues from Argentina, Brazil and Chile, but also from the USA and Europe.

The day ended with banquet, roasting and dancing at a restaurant at the beach of Guarujá.

Many thanks go to the organizer, Prof. Claudio A. Oller do Nascimento, who initiated and organized this Symposium and made financial support from Alcoa Foundation, CEPEMA and LSCP available.

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PUBLICATIONS

ABSTRACTS OF THESES IN PHOTOCHEMISTRY

Andrew McKinley

Photophysics of Light-Switch Ruthenium Complexes and their Interactions with Polynucleotides

School of Chemistry, Newcastle University

Supervisor: Dr. Eimer Tuite

The luminescent DNA probe $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$, ruthenium (*bis*-1,10-phenanthroline dipyrido[3,2-*a*:2',3'-*c*]phenazine), was the first *tris*-bidentate ruthenium complex to be shown unequivocally to intercalate DNA, which it achieves via insertion of the extended dipyridophenazine (dppz) ligand¹. The complex is non-luminescent in aqueous solution but emits strongly in organic solvents, micelles and DNA, with a quantum yield that depends on polarity, H-bonding, and protic ability of the medium. Studies of complexes with methylated dppz derivatives in a range of solvents have shown that a number of solvent factors influence the luminescent switching behaviour, the most intriguing of which is the implication of hydrogen bond formation between the dppz ligand and solvent molecules.

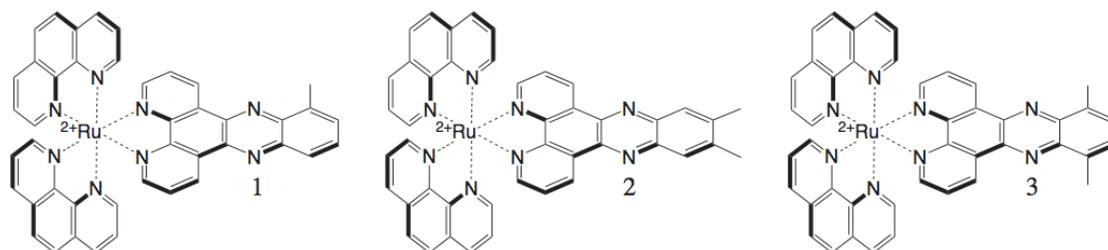


Figure 1: Λ -enantiomers of 10-monomethyl (1), 11,12-dimethyl (2) and 10,13-dimethyl (3) substituted derivatives of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$.

It is generally accepted that the complex binds to DNA by intercalation from the minor groove². However, on binding to polynucleotides, two distinct luminescent lifetimes are observed. This is thought to be a distribution effect in which more closely packed ruthenium complexes are less accessible to solvent quenching and hence have a longer lifetime. This model explains data obtained with most polynucleotides, including $[\text{poly}(\text{dA-dT})]_2$, where a higher proportion of the longer lifetime is observed at low P/D. However, with $[\text{poly}(\text{dG-dC})]_2$ a higher proportion of the shorter lifetime is seen at low P/D and this model no longer fits with observations. Mononucleotide quenching studies, in which only guanosine attenuates the luminescence quantum yield and lifetime of the complex, reveal how guanine may be important in affecting the photophysical properties of the bound complexes. A mechanism is proposed in which luminescence is quenched by an 'electron cascade' between adjacently bound complexes, mediated by the presence of guanine in the polynucleotide sequence.

¹ C. Hiort, P. Lincoln, and B. Norden, *J. Am. Chem. Soc.*, **115**, 3448 (1993).

² E. Tuite, P. Lincoln, and B. Norden, *J. Am. Chem. Soc.*, **119**, 239 (1997).

Finally, luminescence studies of interactions of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ with a range of flavin derivatives were conducted in the presence and absence of polynucleotides, with the aim of uncovering any potential for photoinduced electron transfer in polynucleotides. Although initial studies showed no evidence for electron transfer reactions, a study with linked $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ -flavin complexes binding to polynucleotides shows a possible energy transfer pathway as a function of separation.

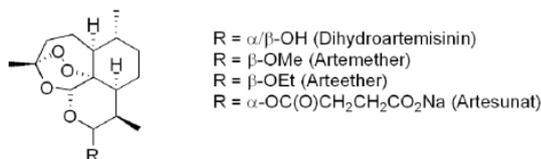
Angela E. Raabe

Synthesis of new Antimalaria-active compounds: Bicyclic perorthoesters with 1,2,4-trioxane structures and adducts combining natural artemisinin and peroxides

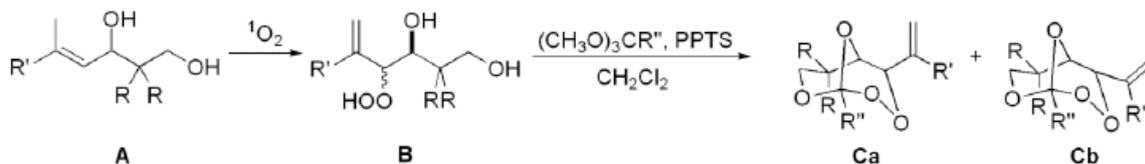
Department of Chemistry, University of Cologne, Köln, Germany

Supervisor: Axel G. Griesbeck

The ene reaction of electronically excited singlet oxygen with allylic alcohols results in β -hydroperoxy alcohols which are suitable building blocks for the synthesis of 1,2,4-trioxanes, the essential sub-structure of the unusual natural antimalaria and antitumor-active artemisinin. This Thesis is part of a campaign to obtain active derivatives of this molecule in order to cope with the expected and lab-proven parasite resistance against artemisinin.



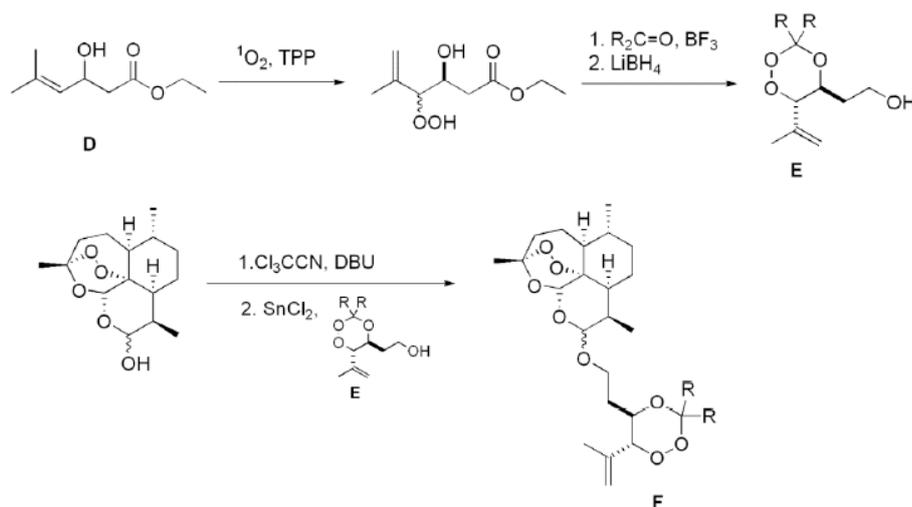
The synthesis of diols **A** as substrates for the photooxygenation was achieved via enantioselective bis-hydroxylation (for 1,2-diols) or diastereoselective aldol addition (for 1,3-diols) with subsequent reduction. In contrast to the results with simple allylic alcohols where high diastereoselectivity was observed due to allylic strain effects, the singlet oxygen photooxygenation of diols **A** resulted in characteristic lower stereoselectivity pattern that represent intra-molecular hydrogen-bonding motifs. The key step in this project was the peroxyacetalization of β -hydroperoxy alcohols using orthoesters as carbonyl equivalents. This step was accomplished using *p*-toluene sulfonic acid (as well as BF_3) catalysts.



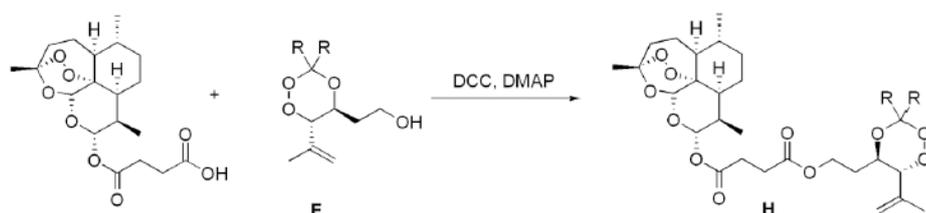
The structure determination was performed by spectroscopic measures together with theoretical calculations (DFT-level) which strongly supported the NMR assignments. The compounds synthesized in this project showed moderate antimalarial activities with about 5% of the artemisinin *in-vitro* activity.

In a second, more ambitious project, the preparation of dyads composed out of the natural artemisinin skeleton and synthetic 1,2,4-trioxanes was envisaged. The non-trivial synthetic steps were realized by selective coupling methods of artemisinin derivatives and non-natural peroxides or, alternatively, by introduction of the peroxide ring system into the artemisinin derivative by photooxygenation and subsequent peroxyacetalization.

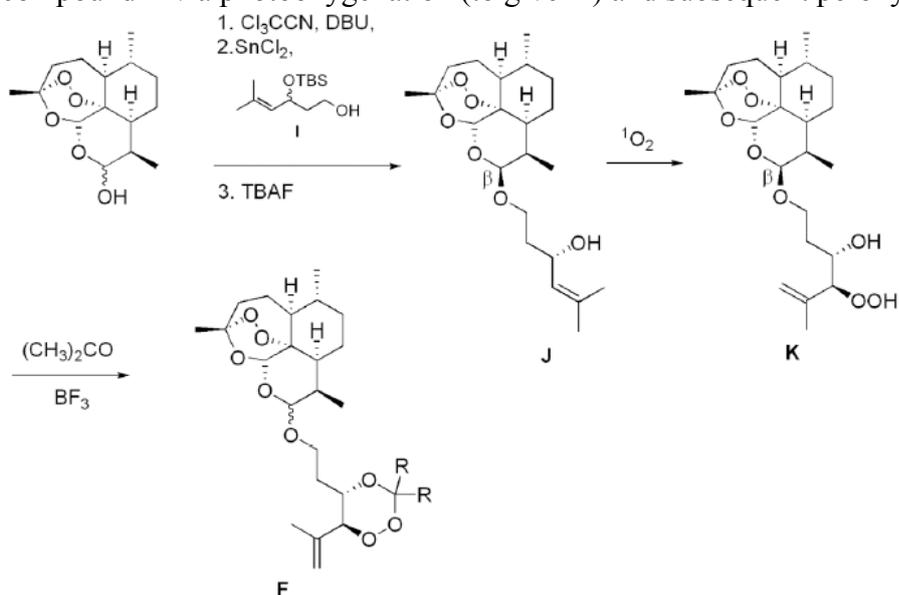
In the first synthetic approach, the aldol adduct **D** was converted in three steps into the 1,2,4-trioxane **E** which was subsequently coupled to dihydroartemisinin.



Esterification of artemesinic acid with the same building block **E** resulted in a dual compound **H** where both trioxane pharmacophors are connected via ester linkage.



In an elegant alternative, the peroxyacetalization was designed as termination of the reaction sequence and was initiated with the artemisinin-linked allylic alcohol **J** which was transformed into the target compound **F** via photooxygenation (to give **K**) and subsequent peroxyacetalization.



Publication:

"Bicyclic Peroxides and Perorthoester with 1,2,4-Trioxane Structures" Axel G. Griesbeck, Dirk Blunk, Tamer El-Idreesy, and Angela Raabe, *Angew. Chem. Int. Ed.* **2007**, *46*, 8883-8886.

Pavel Müller

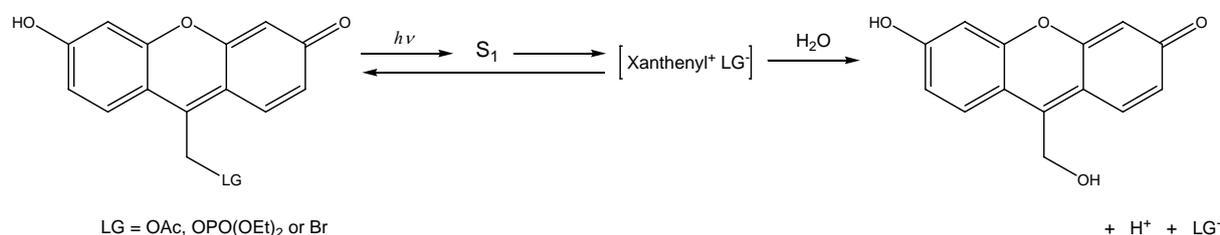
***New Photoremovable Protecting Group Absorbing Above 500 nm:
(6-Hydroxy-3-oxo-3H-xanthen-9-yl)methyl and its Derivatives***

University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Supervisor: Prof. Jakob Wirz, J.Wirz@unibas.ch

A new water-soluble photoremovable protecting group for carboxylic acids and phosphates with high molar extinction coefficients ($\epsilon_{\lambda_{\max}} \sim 25\,000\text{ M}^{-1}\text{ cm}^{-1}$) in the visible region (above 520 nm) was designed and tested. The concept based on the photochemistry of coumarinyl PPG proved to work also for the compounds derived from 6-hydroxy-3-oxo-3H-xanthen-9-yl)methyl. The introduction of an additional aromatic core to the coumarinyl unit resulted in a substantial shift of the absorption towards longer wavelengths and also caused a drop in pK_a of the phenolic protons to about 6, so that the anionic form of the molecule is the prevalent species at neutral pH. This is of advantage since it improves the solubility of these compounds in aqueous media and also because the anionic forms of the cages are even further red-shifted with respect to the neutral ones.

The model cages released the protected bromide, acetate and/or diethylphosphate upon irradiation by visible light in neutral aqueous solutions (the cleavage of the free anions was indicated by a drop in pH and confirmed by NMR).



The quantum yields of photodeprotection of the model compounds were relatively low (< 4.5 %) but still comparable to those of coumarinyl cages. The quantum yields could probably be enhanced by a suitable substitution. The efficiency of the photoreaction is also likely to be higher in the case of cages of other ligands of biochemical interest that are better leaving groups than diethyl phosphate or acetate.

Thesis available online at: http://pages.unibas.ch/diss/2007/DissB_8089.pdf

Arnulf Rosspeintner***Experimental Observations of Diffusional Effects on Photoinduced Electron Transfer Reactions***

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Austria

This work presents the experimental observation and theoretical description of three different experimental manifestations of the complex interplay between the diffusional approach of reactants in liquid solution and their distance dependent intrinsic reaction. In two of the cases the fluorescence quenching rate is monitored when varying either the quencher concentration and solvent viscosity (Stern-Volmer plot) or the driving force of the electron transfer reaction (Rehm-Weller type experiment). It is found, that only the most comprehensive theoretical model, namely differential encounter theory, taking into account the hydrodynamic effect and the solvent structure, in combination with the distance dependent electron transfer model, within the framework of Marcus theory, is capable of reproducing the experimentally observed trends. Additionally, the magnetic field effect on luminescent products of photoinduced electron transfer (exciplex and locally excited state fluorophore) in different solvent environments is investigated and given a theoretical rationale.

Giacomo Bergamini***Photo- and Redox-Active Supramolecular Systems***

Università di Bologna, Italy.

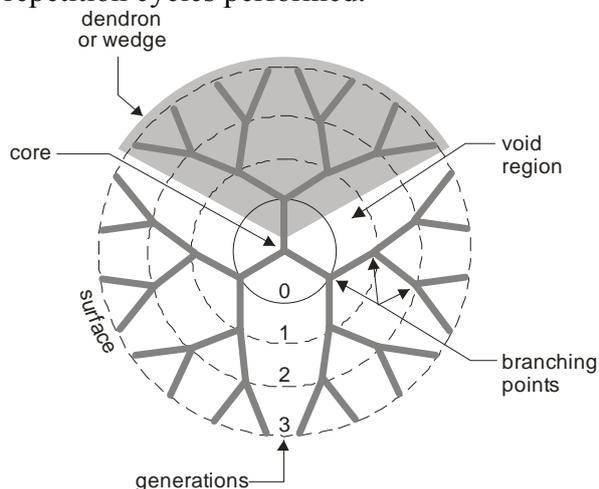
Supervisor: Prof. Vincenzo Balzani

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*”.¹

The supramolecular "bottom-up" approach opens virtually unlimited possibilities concerning design and construction of artificial molecular-level devices and machines. It also became increasingly evident that such an approach can make an invaluable contribution to a better understanding of molecular-level aspects of the extremely complicated devices and machines that are responsible for biological processes.

It should not be forgotten that the development of the supramolecular bottom-up approach towards the construction of nanodevices and nanomachines was made possible by the large amount of knowledge gained in other fields of chemistry. The contributions made by organic synthesis, which supplied a variety of building blocks, and by photochemistry, which afforded a means of investigating the early examples of molecular-level devices and machines (e.g. light-controlled molecular-level tweezers, triads for vectorial charge separation, and light-harvesting antennae) have been particularly important in this regard. In the last few years the concept of molecules as nanoscale objects with their own shape, size and properties has been confirmed by new, very powerful techniques, such as single-molecule fluorescence spectroscopy and the various types of probe microscopy, capable of "seeing" or "manipulating" single molecules. It has been possible, for example, to make ordered arrays of molecules (e.g. to write words and numbers by aligning single molecules in the desired pattern) and even to investigate bimolecular chemical reactions at the single molecule level. The supramolecular systems studied in this thesis are the *dendrimers*.

Dendrimers² are globular, monodisperse macromolecules in which all bonds emerge radially from a central focal point or core with a regular branching pattern and with repeating units constituting the branching points. The term *dendrimer* refers to its characteristic tree-like structure and it derives from the Greek word *dendron* (tree) and *meros* (part). From a topological viewpoint, dendrimers contain three different regions: core, branches and surface. Each repetition synthetic cycle leads to the addition of one more layer of monomers in the branches, called *generation*. Therefore, the generation number of the dendrimer is equal to the number of repetition cycles performed.



Today dendrimers are used or are planned to be exploited in a variety of applications, taking advantage of the great number of functional units that can be incorporated inside them, their tree-like structure containing internal dynamic cavities, their well-defined dimensions close to that of important biological molecules like proteins and bioassemblies, the presence of an internal microenvironment different from the bulk of the solution, and their endo- and exo-receptor properties. As a result, applications ranging from the biological and medical field (artificial enzymes, drug-delivery and diagnostics systems) to nanoengineering (molecular

batteries, light-emitting diodes), optical data transport (fiber optics), catalysis, energy-harvesting devices and mimics of natural photosynthesis are foreseen.³

Currently, dendrimer research is developing swiftly in the direction of highly functional materials. Also in the field of photoactive dendrimers the complexity of the systems has increased enormously. The investigation of dendritic structures functionalized with luminescent groups,⁴ photoswitchable units, energy and/or electron donor-acceptor components and the implementation of such functionalized dendrimers in devices, provide insights into the fundamental processes occurring in such complex systems and in their future applications.

Coupling luminescence with dendrimers is of particular interest since: (i) luminescence signals offer a handle to better understand the dendritic structure and superstructure; moreover, it is possible to monitor the interactions of the macromolecule with other chemical species and with the environment. (ii) Cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting and signal amplification for sensing purposes.

Since dendrimers can be functionalized with multiple chromophoric groups, that are in very close proximity, novel properties can arise compared to the single chromophoric system. Due to the stepwise synthesis, either divergent or convergent, chromophores can be implemented in the dendritic structure with high precision. The presence of multiple chromophores in the same molecule enables the detection of single dendrimer *via* single molecule spectroscopy (SMS), which is particularly interesting for nanotechnology. Furthermore, an increased sensitivity with respect to specific classes of molecules can be established, enabling the detection of very low concentrations of these molecules.

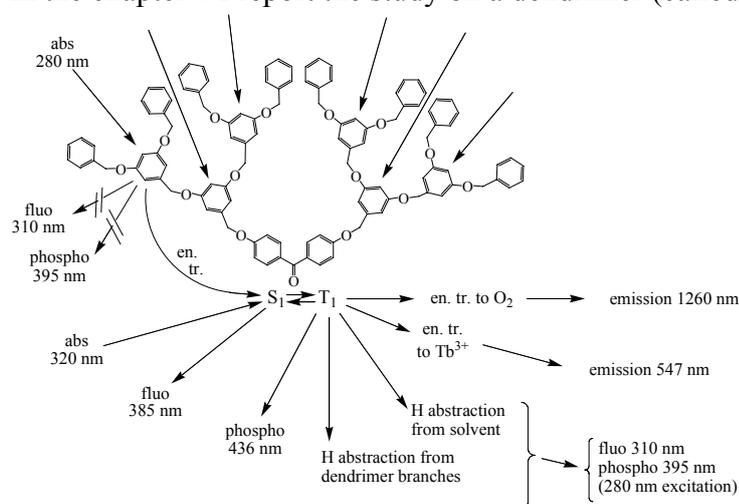
A specific advantage of the dendritic framework is that a microenvironment can be created around a single chromophore. By placing such protective environment around a chromophore its luminescence can be dramatically improved. Dendritic substituents can also promote supramolecular organization of chromophores, e.g. inducing the formation of fibers or doughnut-like structures. The possibility to functionalize chromophores with large dendritic substituents is particularly interesting also for the development of light emitting diodes (LEDs). The dendritic wedges do not only prevent the aggregation of chromophores, thereby reducing the amount of

self quenching, but they also provide a way to improve the solubility of the chromophores in polymers, rendering a more homogeneous blend.

The introduction of photoisomerizable groups, such as azobenzene derivatives, in dendrimers enables the controlled induction of a structural change, especially when those units are attached to the core or implemented in the branches. If attached at the periphery, these photoisomerizable groups, can be used to “close” the surface of a dendrimer by means of a photoinduced increase of steric hindrance at the periphery. This type of dendrimers can be used as carriers of small molecules, while a controlled release of those guest molecules is possible using light, which induced the isomerization from *cis* to *trans*. In addition, azobenzene-functionalized materials are widely used in the field of datastorage.

Dendrimers can be functionalised, in their different topological regions, with luminescent moieties: photoactive units can also be non-covalently hosted in the cavities or associated on the dendrimer surface.

In the chapter 4 I report the study on a dendrimer (called **BBG2**) consisting of benzophenone as a



core, and branches that contain 1,3-dimethoxybenzene units (Fréchet-type branches). The photochemical and photophysical behavior of the dendrimer can be schematically summarized by the reported scheme.

In dendrimer **BBG2** the fluorescent S_1 excited state of the dimethoxybenzene units is completely quenched via energy transfer (presumably by a resonance mechanism) to yield the S_1 excited state of the benzophenone-type core, that can also be directly populated by light absorption ($\lambda_{ex} =$

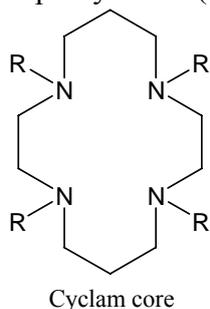
320 nm). The S_1 excited state of the core lies slightly above the correspondent T_1 excited state. The two states, in fact, are in thermal equilibrium at 298 K. However, the T_1 excited state of the core is rapidly deactivated via intramolecular hydrogen abstraction. In a rigid matrix at 77 K, where hydrogen abstraction is prevented, the phosphorescence band of the benzophenone moiety is observed for **BBG2**. Since the rate of the photoreaction in 1:2 v/v propan-2-ol/acetonitrile is not much higher than that in neat acetonitrile for **BBG2**, the intramolecular hydrogen abstraction in the dendrimer competes with the intermolecular one. It should also be noted that the occurrence of the hydrogen abstraction reaction causes the disappearance of the benzophenone core phosphorescence, and therefore the revival of the dimethoxybenzene fluorescence and phosphorescence upon 280 nm excitation. In aerated solution, the photoreaction rate of **BBG2** is substantially smaller, showing that there is a competition on the T_1 excited state between hydrogen abstraction and dioxygen quenching. The sensitized dioxygen emission observed for aerated acetonitrile solutions of **BBG2** shows that the quenching is due, at least in part, to energy transfer.

The sensitized Tb^{3+} emission observed upon excitation at 320 nm of solutions containing **BBG2** and $Tb(CF_3SO_3)_3$ shows that the T_1 excited state of the core can transfer energy to the metal ion.⁵ **BBG2** is indeed an outstanding example of a chemical compound that can be used to illustrate most of the processes that are discussed in an entire photochemical course.

Continuing the studies on energy transfer processes in dendrimers, we have investigated the photochemical and photophysical behaviour of two dendrimers consisting of a benzophenone

core and branches that contain four (**BNG1**) and eight (**BNG2**) naphthalene units at the periphery (chapter 5). In both dendrimers, excitation of the peripheral naphthalene units is followed by fast singlet-singlet energy transfer to the benzophenone core, but on a longer time scale a back energy transfer process takes place from the triplet state of the benzophenone core to the triplet state of the peripheral naphthalene units. Selective excitation of the benzophenone unit is followed by intersystem crossing and triplet-triplet energy transfer to the peripheral naphthalene units. This sequence of processes, which is made possible by the preorganization of photoactive units in a dendrimer structure, can be exploited for several purposes. In hydrogen donating solvents, the benzophenone core is protected from degradation by the presence of the naphthalene units. In solutions containing $\text{Tb}(\text{CF}_3\text{SO}_3)_3$, sensitization of the green Tb^{3+} luminescence is observed on excitation of both the peripheral naphthalene units and the benzophenone core. Upon excitation of the naphthalene absorption band (266 nm) with a laser source, intradendrimer triplet-triplet annihilation of naphthalene excited states leads to delayed naphthalene fluorescence ($\lambda_{\text{max}}=335$ nm), that can also be obtained upon excitation of the benzophenone core at 355 nm (energy up-conversion).⁶

An important property of dendrimers is the presence of dynamic internal cavities. Therefore we have studied two novel dendrimers consisting of a cyclam core with appended four dimethoxybenzene and eight naphthyl units (**CyG1**) and twelve dimethoxybenzene and sixteen naphthyl units (**CyG2**).



The investigated dendrimers, reported in the chapter 6, show fluorescence bands that can be assigned to naphthyl localized excited states ($\lambda_{\text{max}} = 337$ nm), naphthyl-amine exciplexes ($\lambda_{\text{max}} = 470$ nm) and, for **CyG2**, naphthyl excimers (λ_{max} ca 390 nm). The intensity and shape of these bands are strongly affected by coordination of Ni(II), Co(II) and Cu(II), as nitrate salts, to the cyclam core. Complexation with these metal ions has a double-faced effect: on one hand, it can increase naphthyl localized emission and suppress exciplex emission, engaging nitrogen lone pairs of cyclam; on the other hand, it can quench this fluorescence by offering additional deactivation pathways to the naphthyl

singlet excited state via energy or electron transfer processes. Complexation with Cu(II) causes not only changes in the relative intensities of the fluorescence bands, but also the appearance of a new absorption band in the near UV spectral region. Analysis of the titration curves has allowed us to obtain clear evidence for formation not only of 1:1 species, but also 1:2 metal to ligand species. **CyG2** shows a clear preference, compared to **CyG0**, in forming complexes with 1:2 metal to ligand stoichiometry. This counterintuitive effect demonstrates that the bulky dendrons appended to the cyclam core do not hinder, but favour the formation of complexes with 1:2 metal to ligand stoichiometry.⁷

In a further effort to explore the potentiality of cyclam-based fluorescent dendrimers as ligands for metal ions (and thus as fluorescent sensors), we have synthesized a novel dendrimer (**BisCyc**) based on two covalently linked cyclam units as a core appended with six branches, each one consisting of a dimethoxybenzene and two naphthyl units. As for the monocyclam dendrimers, also the **BisCyc** exhibits three fluorescence bands assigned to naphthyl localized excited states ($\lambda_{\text{max}} = 336$ nm), naphthyl excimers (λ_{max} ca 390 nm), and naphthyl-amine exciplexes ($\lambda_{\text{max}} = 510$ nm). Titration with H^+ , Zn^{2+} , and Cu^{2+} causes strong changes in the emission spectrum and, in the case of Cu^{2+} , also in the absorption spectrum. Clear evidence for formation of 1:1 (**BisCyc**. H^+), $[\text{Zn}(\text{BisCyc})]^{2+}$, $[\text{Cu}(\text{BisCyc})]^{2+}$) and 2:1 (**BisCyc**. 2H^+), $[\text{Zn}_2(\text{BisCyc})]^{4+}$, $[\text{Cu}_2(\text{BisCyc})]^{4+}$) species has been obtained. The three luminescence bands and, in the case of Cu^{2+} , also an absorption band, offer the way to monitor not only the metal-ligand coordination process, but also its consequences on the interaction between the naphthyl units contained in the dendritic branches. We would like to note, however, that while the availability of dendrimers

possessing a well defined ligand unit, like cyclam, opens the way to the construction of mixed-(dendritic)ligand complexes, dendrimers containing two cyclam units can be used, in principle, to construct dendrimers containing two different types of metal ions.¹⁰

In chapter 8 I report how the luminescent cyclam-based hosts **CyG0** and **CyG2** can be assembled with the luminescent metal complex $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ by a proton-driven process that causes strong changes in the luminescence properties. In the $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \text{CyG0}\}$ and $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \text{CyG2}\}$ adducts formed in this way, very efficient energy transfer takes place from the naphthyl units of **CyG0** and **CyG2** to the metal complex.

I have also shown that the $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \text{CyG0}\}$ and $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \text{CyG2}\}$ adducts can be disrupted by two distinct chemical inputs, namely addition of a base, yielding the starting species $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ and **CyG0** or **CyG2**, or further addition of acid, with formation of $(\text{CyG0} \cdot 2\text{H})^{2+}$ or $(\text{CyG2} \cdot 2\text{H})^{2+}$ and protonated forms of $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$. Such processes cause strong changes in the luminescent properties. In particular, in the case of $\{[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-} \cdot (2\text{H}^+) \cdot \text{CyG2}\}$ there are two optical output channels, emission at 335 and 680 nm, that behave as XOR and XNOR logic gates, respectively.

The system investigated in this chapter is an example of a light harvesting antenna in which the energy collecting units can be reversibly assembled to/disassembled from the dendrimer core. This behavior introduces more flexibility in view of the construction of systems useful for artificial photosynthesis.¹¹

The four dendritic systems presented in the chapter 9, based on four different luminophores, namely terphenyl (**T**), dansyl (**D**), stilbenyl (**S**), and eosin (**E**), provide representative examples of different mechanisms of fluorescent depolarization.

In the first case, the fluorophore **T** constitutes the core of the dendrimer and fluorescence depolarization is due to global rotation of the dendrimer. In the second and third cases, multiple **D** and **S** luminophoric units, respectively, are appended in the periphery of poly(propylene amine) dendritic structures. However, the photophysical properties of **D** and **S** are so different that energy migration is very efficient only among the **S** units. In the more viscous mixtures of solvents, fluorescence depolarization occurs mainly by local motion for the **GnD** family and by energy migration for the **G2S** dendrimer. In the fourth case, the investigated luminophore (**E**) is non-covalently encapsulated in cavities of a fourth generation poly(propylene amine) dendrimer **G4B**, containing 1,2-dimethoxybenzene (**B**) units at the periphery. In this case, the study of fluorescence anisotropy of eosin evidenced that eosin rotation inside **G4B** dendrimer cavities is restricted and that when, as an average, more than one eosin is encapsulated inside a dendrimer, efficient energy migration takes place.¹²

Fluorescence anisotropy reveals once more a very useful tool to investigate dendrimer structures and energy migration processes.

In the chapter 11 it is reported a study that I performed in the laboratory of Prof Frans De Schryver, in Leuven, Belgium. We used defocused wide-field imaging, obtained using a wide-field fluorescence microscope, in combination with an extremely robust perylendiimide dye to study rotational motion of the dye in a polymer with a T_g close to room temperature. We demonstrated the potential of defocused wide-field fluorescence microscopy to monitor molecular rotational diffusion in a glassy polymer. Due to the good signal-to-noise ratio of the fluorescence images, 3D reorientation of molecular dipole moment could be followed. Using the full 3D rotation avoids the introduction of analysis artifacts. The data clearly evidence non-directional molecular rotation, resulting from random polymer relaxation. We showed that the autocorrelation function for the rotation of different probe molecules can vary greatly, resulting in large differences in rotational correlation times. This is due to the highly poly-disperse PMA

matrix used. The advantage of wide-field imaging (parallel data collection of many molecules) allows us to probe spatially heterogeneous dynamics on the sub-1 μm scale, which is a promising result for investigating local environmental changes in phase separation processes or for investigating changes in viscosity during polymerization reactions. The 3-D rotational correlation function could only be fitted bi-exponential. This might relate to different relaxation regimes predicted by polymer theories.⁸

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Yong Sheng Zhao

Preparation and Optoelectronic Properties of Organic Nanomaterials

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Supervisor : Prof. Jiannian Yao

Nanomaterials have attracted extensive investigation due to their unique optoelectronic properties and their potential applications in optoelectronics, catalysis, energy and information storage, etc. However, most of the researches are focused on inorganic semiconductor materials. The controllable constructions of organic nanostructures are more challenging because of their weak intermolecular interactions and low melting point. Organic materials, due to their optical tunability, high luminescence efficiency, and self-assembly property, can serve as effective building blocks in the future miniaturized optoelectronics. Therefore, the fabrication and application of organic nanomaterials are of great scientific and technological significance.

In this thesis, organic low dimensional materials with controllable morphologies and properties were fabricated from several opto-functional compounds with some groping techniques. The photonic and electronic properties of the as-prepared organic nanomaterials were investigated in detail.

1. Photonic and optoelectronic properties of single crystalline 1D nanomaterials and nanodevices based on small organic molecules: During the past decade, ever increasing attention has been paid to one-dimensional (1D) nanomaterials, because the two-dimensional quantum confinement effect makes them promising as building blocks for nanoscale devices, such as logic gates, photodetectors, chemical sensors, and so on. One of the emphases of this thesis lies in the preparation and photonic/electronic properties of crystalline organic 1D nanomaterials. An adsorbent-assisted physical vapor deposition (PVD) method was developed to prepare organic nanowires with high uniformity. Adsorbents were introduced into the PVD systems to improve the size uniformity of organic nanomaterials.

A. Optical waveguide and ultraviolet laser based on 2, 4, 5-triphenylimidazole (TPI) nanowires prepared with adsorbent-assisted PVD method. With the adsorbent-assisted PVD method, single crystalline TPI nanowires were prepared. The fluorescent emission spectra of the nanowires at room temperature were remarkably narrowed, which are usually observed only under cryogenic conditions. The vibrational fine structures become more pronounced with the decrease of diameter. The as-prepared nanowires showed microcavity effects, and single wire waveguide and UV laser were also realized.

B. Fabrication of electroluminescent (EL) and field emission (FE) devices from tris(8-hydroxyquinoline)aluminum (Alq₃) nanowires. Single crystalline Alq₃ nanowires were prepared with the adsorbent-assisted PVD method, and the Alq₃ nanowires were fabricated to EL and FE devices. The photoluminescent vibrational fine structures emerge and become pronounced with the increase of the excitation energy. Both the EL and FE properties enhance considerably with the decrease of the wire diameter.

C. Multicolor emission from ordered assemblies of organic 1D nanomaterials. Multicolor emission, especially red-green-blue (RGB) emission is essential to display and flat screen. Generally, multicolor emission is realized with thin films of dye-doped polymers or blends of polymers. We demonstrate that it is also possible to achieve multicolor emission from the crystalline organic nanoribbons and the hierarchical assemblies. The selected model compound 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (PPCP) is a well known blue light-emitting dye. After being fabricated to crystalline nanoribbon assemblies, PPCP displayed multicolor emission property, i.e., blue, green, and red emissions will be achieved respectively by exciting the same sample with appropriate wavelengths.

D. Tunable emission from binary organic 1D nanomaterials. The adsorbent-assisted PVD method was extended to doped binary organic systems. 1,3,5-triphenyl-2-pyrzoline (TPP, a blue emitter for EL use), and rubrene, a good orange dye widely used as the dopant in OLEDs, were chosen as the model compounds, which were fabricated into uniformly doped crystalline nanorods and nanowires. The emission color of the binary nanomaterials can be readily tuned by modulating the molar ratio of the two compounds, and white-light emission was obtained when proper molar ratio was adopted.

2. Self-assembly and optoelectronic properties of organic functional molecules: For the future miniaturized optoelectronics, it is a key task to fabricate the nanoscale interconnects with unique photonic and electronic properties. Self-assembly is an effective way to the

construction of organic nanostructures because the intermolecular non-covalent interactions allow them to aggregate orderly. In my work, the assembly of some small conjugated organic molecules and organic heterocyclic molecules were investigated. The optical, electronic, and photonic properties of the assembled structures were also studied.

A. Optical waveguide based on organic microtubes. Optical nanowaveguides is a kind of important interconnects, which can propagate and manipulate lights efficiently on the sub-wavelength scale. In the past couple of years, inorganic semiconductor nanowires have been widely utilized as optical waveguide and optically driven lasers. In my work, we prepared two kinds of microstructures with rectangular and square cross-sections, respectively from a low-molecular-weight organic compound, 9,10-bis(phenylethynyl)anthracene (BPEA), and extended the application of miniaturized sub-wavelength optical waveguide from solid wires and ribbons to hollow tubular structures. The prepared 1D BPEA microstructures can serve as both single tube/rod and inter-tubes/rods active optical waveguides. The air medium inside the tubes can change the waveguide behaviour and help to reduce the optical loss.

B. Construction of submicrotubes from the self-assembly of 2, 4, 5-triphenylimidazole (TPI): Single crystalline nano- and submicrotubes were prepared from the self-assembly of an organic heterocyclic compound, 2, 4, 5-triphenylimidazole (TPI). The length and diameter of the TPI tubes can be readily controlled, and the tubes have intensive luminescence, size-dependent optical properties and good stability, which allow them to find potential applications in novel optical and optoelectronic devices.

C. Modification of metal nanomaterial surfaces with organic functional molecules: The metal (copper, silver and gold) nanostructures such as nanorods, wires and particles were first synthesized with low-temperature liquid methods. The surfaces of the metal nanomaterials were then modified with organic molecules to form metal/organic core/sheath nanocomposites. The shape and size of the nanocomposites can be modulated readily by varying the morphology of the metal core. The sheath can protect the copper nanomaterials from being oxidized. Interestingly, the optical properties of the shell can be tuned by just changing the size of the metal cores.

D. Self-assembly of 4,5-diphenylimidazole (DPI), from single molecules to 2D building blocks to higher-order mesostructures on metal surfaces: The coordination property of organic heterocyclic molecules with transition metals was utilized to construct ordered hierarchical mesostructures at metal surfaces. DPI was induced to self-assemble into higher-order mesostructures at copper-solution interface. By changing the assembly conditions, DPI was controlled to assemble into different morphologies with diverse properties. The mesostructures can endow the copper surfaces with novel superhydrophobic property and inhibit the corrosion of copper significantly.

Zsombor Miskolczy

Interaction of fluorescent probes with micelles and molecules capable of hydrogen bonding

University of Debrecen. Workplace: Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary

Supervisor: László Biczók

Fluorescent compounds are widely used as probes to examine the structure, dynamics and microenvironment in biological and microheterogeneous systems. In order to develop the most suitable optical probe for different purpose, it is of pivotal importance to unravel the major factors controlling the kinetics of the excited state deactivation pathways.

This dissertation revealed how the local polarity and the interaction with hydrogen-bond donors or acceptors affect the photophysical properties of four heterocyclic compounds: 2-hydroxy-substituted Nile Red dye (HONR), ellipticine, 6-methylellipticine and lumichrome.

Because of the high sensitivity of its fluorescence to the local polarity, HONR proved to be an excellent probe for the study of the ionic liquid aggregation in aqueous solution and the subtle changes of the interfacial layer. We demonstrated that ionic liquids could be used to modify in a controlled fashion the properties of the conventional micelles. Smaller aggregation number and critical micelle concentration were found for 1-alkyl-3-methylimidazolium bromide ionic liquids than for the corresponding alkyltrimethylammonium bromides in water, whereas the fractional charge on the micelle was very similar for both types of cationic surfactants.

The detailed mechanism and the kinetics of the HONR fluorescence quenching by hydrogen bond acceptors were elucidated with the combined analysis of the steady-state and time-resolved spectroscopic data. The relative contribution of the competing reaction steps changed significantly with the basicity of the additive and the solvent polarity.

The effect of hydrogen bond acceptors on the deactivation of singlet-excited ellipticine, a pyridocarbazole type plant alkaloid, was also studied. Deprotonation in the ground state was brought about only by the interaction with two F^- anions in acetonitrile. The fluorescence band of the 1:1 complex with F^- or CH_3COO^- showed large Stokes shift implying significant proton displacement upon excitation along the hydrogen bond. The binding of a stronger base, N-methylimidazole, to the excited ellipticine proved to be reversible and weakly exothermic in acetonitrile indicating the lack of correlation between the energy of the excited hydrogen-bonded complex and the basicity for different type of hydrogen-bond acceptors. The complex of the strongly basic 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) did not fluoresce because fast proton transfer occurred in the excited state.

Photophysical parameters of ellipticine alkaloid were compared to those of its 6-methyl derivative in various solvents. Since both compounds emitted dual fluorescence in methanol and ethylene glycol, the band peaking at low energy could not be due to a 'quinoid-like' tautomer, which had been proposed for olivacine, a compound differing from ellipticine only in the position of a methyl group, but originated from the photoinduced protonation by the solvent. The mechanism and kinetics of the processes undergoing in the excited-state in the presence of OH^- were revealed in methanol.

Systematic studies of the effect of anions on the spectral characteristics of lumichrome, the major product of riboflavin photodecomposition and biodegradation, showed that this compound may be utilised as a highly sensitive, off-the-shelf fluorescent probe. The remarkably strong 1:2 binding of F^- or CH_3COO^- anions to ground state lumichrome in acetonitrile and the interaction with 1:1 stoichiometry in 1–6 M water/acetonitrile mixtures led to a significant bathochromic displacement in the absorption and fluorescence spectra as well as a concomitant marked fluorescence enhancement due to the formation of an isoalloxazine-type electron distribution.

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Fadi Hatoum

Photodecarboxylative Additions to Phthalimides and their Application in the Synthesis of AKS-186 and its Analogues

Dublin City University. Workplace: Chemical & Pharmaceutical Sciences, Dublin 9, Ireland

Supervisor: Dr. Michael Oelgemöller

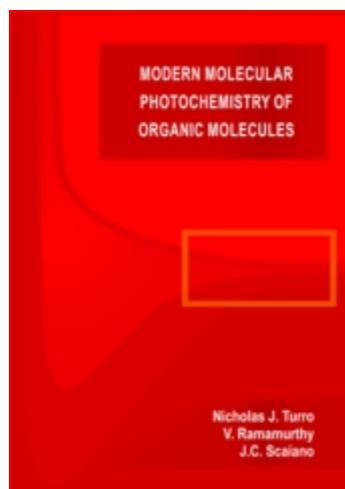
Photochemical methods have been widely neglected by industry for the search of novel pharmaceutical lead compounds. The photodecarboxylative addition of various carboxylates to phthalimides has been developed in our group as a powerful access to hydroxyl- and methylene-isoindolones. Likewise, the *intramolecular* version yields the corresponding cyclisation products.

In this thesis the *intermolecular* version, *i.e.* the photodecarboxylative addition of carboxylates to phthalimides, has been further investigated. Various heteroatom-substituted carboxylates have been studied in order to establish a mechanistic understanding of the photoinduced electron transfer processes involved. *N*-methylphthalimide was used as a model substrate and was irradiated at $\lambda = 300$ nm in aqueous acetone and in the presence of excess amounts of potassium carboxylates, the latter generated from the corresponding carboxylic acid and potassium carbonate. The evolution of carbon dioxide was tested using barium hydroxide solutions and was deemed positive when barium carbonate precipitation was formed. Among the carboxylates used were alkyl-, benzyl- and heteroatom-substituted carboxylates. Alkylated amino acid derived carboxylates solely underwent photoreduction whereas *N*-acylated amino acid readily furnished the desired addition products. To investigate the possibility of deactivation by certain electron-donors, various phthalimides with potential electron-donor substituents in the *N*-side chain have been studied. In these cases potassium propionate served as model carboxylate.

In an extension of the decarboxylative addition, alkyl benzoylformates were irradiated in the presence of sulphur-containing carboxylates and the corresponding addition products were obtained in moderate to good yields. Due to their less favourable electrochemical properties, these compounds do not undergo photoinduced electron transfer reactions with alkyl-, benzyl- or oxygen-containing carboxylates, respectively.

The optimised irradiation conditions were applied to the synthesis of AKS-186 and its derivatives. AKS-186 has demonstrated promising cardiovascular drug activities and became readily accessible from *N*-(4-acetoxybenzyl)phthalimide using the developed photochemical method as key-step. Depending on the nature of the chosen carboxylate the addition products were obtained in poor to good yield of 10-76%. Subsequent dehydration/deprotection gave the desired target compounds in good to excellent yield of 70-96%.

BOOKS

Modern Molecular Photochemistry of Organic Molecules

Nicholas J. Turro, V. Ramamurthy and Juan Scaiano
Palgrave Macmillan
28 Apr 2009

Description

A complete revision of Turro's classic text, *Modern Molecular Photochemistry*, which has been the standard of the field for three decades. It presents a clear introduction to organic chemistry and goes on to cover the mechanisms of organic photoreactions and the photochemistry of the basic functional groups of organic chemistry.

Contents

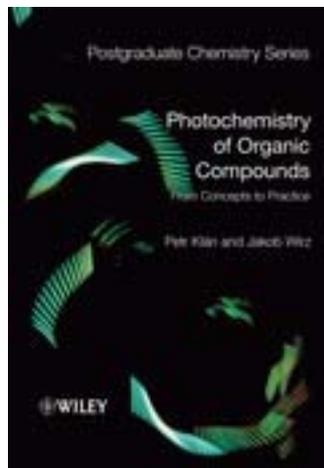
Introduction and Overview
Electronic, Nuclear and Spin State of Electronically Excited States
Transitions Between States
Radiative Transitions Between States
Radiationless Transitions Between States
Theoretical Organic Photochemistry
Energy and Electron Transfer Process
Mechanistic Organic Photochemistry
Photochemistry of Carbonyl Compounds
Photochemistry of Olefins
Photochemistry of Aromatics
Medium Effects of Photochemical Processes: Organizes and Constraining Media
Oxygen in Photochemistry
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Author Biographies

NICHOLAS J. TURRO has been the William P. Schweitzer Professor of Chemistry at Columbia University, USA, since 1964. He is the author of *Modern Molecular Photochemistry*, the standard text in the field, and has published over 750 research papers in established scientific journals. He is a member of the National Academy of Sciences and the American Academy of Arts and Sciences.

V. RAMAMURTHY is Bernaud Bauss Professor of Organic Chemistry at Tulane University, New Orleans, USA.

JUAN C. SCAIANO is Professor of Organic Chemistry at the University of Ottawa, Canada.

BOOKS**Photochemistry of Organic Compounds: From Concepts to Practice**

Petr Klán and Jakob Wirz
John Wiley and Sons
February 2009

Detailed description

Organic Photochemistry can broadly be divided into two, covering either the physical organic chemistry aspects of the subject or the practical application of photochemistry in the synthesis of new molecules. Photochemistry can offer the synthetic organic chemist a high yielding, clean and efficient reaction process, and can give access to structures or stereochemistry that are difficult to prepare in other ways.

This new volume in the Postgraduate Chemistry Series covers synthetic organic photochemistry at postgraduate student and research level. It provides a thorough overview of this important and exciting area of research, demonstrating the underlying principles of synthetic organic photochemistry and, by reference to a range of organic reaction types, its effective use in the synthesis of new organic materials.

Written for postgraduate students and those beginning their research careers, the book will also serve as a handy reference for more experienced workers.

From the contents

1. Introduction (4 pages).

(historical sketches; OP as a scientific field; photochemistry in nature; etc.).

2. A brief introduction to molecular organic photochemistry (10 pages).

Light; Spin; Electronic excited states; Radiative transitions; Non-radiative transitions; Energy and electron transfer; Excite state kinetics etc.

3. Techniques and methods in practical organic photochemistry (40 pages).

a) Optical sources; photochemical benches and reactors.

b) The quantum yield measurement; actinometry.

c) Transients and the laser flash spectroscopy.

d) Two-photon excitation.

e) Single molecule spectroscopy.

f) Low temperature studies; matrix photochemistry.

4. Primary photochemical reactions (110 pages).

(information based on a structural and electronic character of organic compounds; experimental facts; mechanistic considerations; examples, chemical and quantum yields, selectivity; synthon approach (?)).

Mechanisms of photochemical reactions (types; a brief and cumulative (graphical) introduction).

- a) Alkanes and cycloalkanes.
- b) C=C; C^oC; dienes
- c) C=N; N=N;
- d) Carbonyl compounds; thiocarbonyl compounds
- e) Aromatic compounds; heterocyclic compounds
- f) C-Hal; C-N; C-Si;
- g) Singlet oxygen.

5. Synthetic, applied and industrial organic photochemistry (70 pages).

Preparative photochemistry; chiral photochemistry; photochromism; photoremovable protecting groups; cage compounds; supramolecular photochemistry; solid state; materials; surfaces; organic solar cells; biochemical and medicinal applications, etc.

CONFERENCE REPORTS

XXII IUPAC Symposium on Photochemistry July 28– August 1, 2008, Gothenburg, Sweden

The Symposium was a real success, with 430 participants from 51 Countries. In spite of the gorgeous weather, all sessions (there were always three parallel sessions) in the modern Convention Centre were very well attended. There were 7 plenary lectures by Vincenzo Balzani (University of Bologna, Italy), Harry Gray (California Institute of Technology, USA), Leif Hammarström (Uppsala University, Sweden), Stefan Hell (Max-Planck-Institut für Biophysikalische Chemie, Germany), Masahiro Irie (Rikkyo University, Japan), Josef Michl (University of Colorado, USA), Atsuhiko Osuka (Kyoto University, Japan), and Eric Vauthey (University of Geneva, Switzerland). The majority of plenary lectures and many of the invited and selected oral lectures, directly or indirectly, addressed the problem of solar energy conversion in view of the climate change and energy crisis confronting the world. There were 12 invited lectures and 96 selected oral presentations organized by scientific areas. There were also 414 posters that could hang during the whole duration of the Symposium. The discussions after the lectures and during the poster sessions were very lively. Many colleagues and students had thus opportunity of presenting their results.

The areas covered during the week were very wide, ranging from spectroscopy of molecular entities and of nanostructures, photochemistry of drugs, photochemistry in microheterogeneous media, fluorescence markers and sensors of various chemicals, supramolecular units mimicking antennas and reaction centres of photosynthesis, photopolymerizations and photochemistry in solid state, theoretical considerations and calculations of excited states, spectroscopic studies with biological photosensors, and some others. There were also several exhibitors of instruments whose booths were very well visited.

The Plenary Lecture offered by Stephan Hell was sponsored by the photochemistry and photobiology societies owning the Journal *Photochemical and Photobiological Sciences* (PPS) and produced by the Royal Society of Chemistry. Michael Wasielewski received the prestigious Porter Medal, awarded by the three photochemistry Societies, *i.e.*, IAPS (Inter-American Photochemical Society), EPA (European Photochemical Association), and APA (Asian Photochemical Association) and gave a plenary lecture on this occasion. There were also EPA Prizes for young photochemists, awarded to Maria Abrahamson (Sweden) and Alex Fürstenberg (Switzerland).

During the lunch breaks several meetings of various Committees took place, such as that of the presidents of the photochemical societies, the Sub-Committee on Photochemistry of IUPAC and the task force working on the Project on Fluorescence Standards from IUPAC. The EPA (European Photochemical Association) had its general assembly on Thursday afternoon.

All in all, the Conference was well organized and very successful, both scientifically and socially and once more the photochemistry community showed its strength and vitality. Many young fellows enjoyed the scientific discussions and showed their wonderful results. The boat trip to the Archipelago was wonderful and the medieval dinner in the dungeons of the Fortress made us have a taste of the Swedish past.

During the Conference it was announced that the next IUPAC Symposium on Photochemistry will be held in Ferrara, Italy, in July 2010. Scientific Chair is Franco Scandola. It was also suggested that the Symposium in 2012 should be held in Coimbra, Portugal, and that the scientific chair should be Hugh Burrows from Portugal.



Silvia E. Braslavsky

August 12, 2008

Cornelia Bohne (Canada, President of the Inter-American Photochemical Association) gives the Porter Medal in the name of the three Photochemical Associations (Inter-American, Asian, and European) to Michael Wasiliewski (USA).



Alexander Fürstenberg (Geneva, Switzerland) receives the European Photochemical Association (EPA) PhD Prize, from the hands of the EPA President, Dimitra Markovitsi.



Maria Abrahamsson (Uppsala, Sweden) gives the lecture after receiving the European Photochemical Association (EPA) PhD Prize.

CONFERENCE REPORTS

HRSMC Summer School "Photochemistry 2008: Fundamentals and Applications"

May 31 – June 4 2008, Castle Vaeshartelt, Maastricht, The Netherlands

A bright spot for enlightening discussions

Castle Vaeshartelt, a short distance outside the city of Maastricht, was chosen by the Holland Research School of Molecular Chemistry (HRSMC) to be the venue of this year's summer school on photochemistry and photophysics. Under the auspices of the European Photochemistry Association, a collective of 51 students and seven speakers from all over the world gathered at this splendid location. The inspiring premises of the historic Castle instantly showed their effect on the participants. Intense scientific (and also more worldly) discussions came up quickly, certainly to the pleasure of the organising staff. Naturally, they had put special emphasis on stimulating exchange between all participants, students and speakers alike. Not only had poster sessions— of course a very standard part of scientific meetings – been organised, but also discussion sessions directly following the lectures. Despite not all participants using these excellent occasions to clarify questions, generate new ideas, and get into contact with their fellow participants, a very open and stimulating atmosphere was created.

And when eventually the Maastricht bus drivers went on strike, there was literally no other way than to concentrate on the broad range of state-of-the-art topics on photochemical and photophysical research presented by the invited speakers. The talks ranged from pure photochemistry (Axel Griesbeck) to more physical fields such as single-molecule and ultrafast-spectroscopy methods (Christina Flors, Marloes Groot), and organic light emitting devices (Marc Thompson), as well as a combination of both (Luis Liz-Marzan: spectroscopy of small metal particles; Maurice Alders: medical photonics). Finally, Ivano Tavernelli had to cope with the difficult task of introducing the participants to methods of computational photochemistry, which he excellently managed. Thus, the participants had an excellent possibility to broaden their scientific horizon far beyond their own respective projects. In summary, the school was a great success and very positively received by the participants. Read some impressions below:

Maurice Alders from Amsterdam Medical Center presented a special medical photonics lecture, which highlighted new techniques of using nanoparticles for oncological investigations, or Raman spectroscopy for medical analysis. In this presentation I found a number of applications for techniques we use in our lab. The other presentation most interesting to me was given by Luis Liz-Marzan on nanoparticles, from which I learnt how to handle these particles in different specific environments. Furthermore, I very much enjoyed the location of the summer school as well as the very active collaboration between speakers and students! Elisabeta Cecilia Vidami Negoescu

The summer school was highly interesting to me for not only acquiring advanced knowledge about ultrafast laser science, but it also furthered my understanding on medical photonics, nanomaterials, and LEDs. I also learnt different techniques for steady-state and time-resolved absorption and fluorescence measurements. Thus, I am very grateful for having had the opportunity to take part in the great scientific discussions with experts in different fields and with the scientific colleagues who come from different parts of the world. The lectures were of highest quality, and in addition to them, discussion sessions were organised where more detailed questions could be discussed and answered. These discussion sections were highly appreciated

by the participants. Finally, I wish to highlight the efforts of the organising team who made this summer school very successful, both in terms of scientific discussions and social event. I'm certainly waiting for the next summer school! Viruthachalam Thiagarajan

Particularly interesting for me was the topic on nonlinear spectroscopy introduced by Marloes Groot from Vrije Universiteit Amsterdam. The sophisticated nature of the setup used for ultrafast spectroscopy was explained, and thus the talk was a useful introduction for those planning to do such experiments. The lectures provided a good basis to the nonspecialist for further study into this method of investigating ultrafast processes. Besides that, I very much enjoyed the lectures of Luis Liz-Marzan, who presented research on noble-metal nanoparticles and photophysical studies that can be conducted on them. His talks were an excellent introduction for those people not working in the field and a nice refresher for those that deal with nanoparticles in their daily work. Linh Tran

Financial support of the HRSMC Summer School 2008 by the following companies is gratefully acknowledged: HAMAMATSU, Ciba, Unilever, Pico Quant, Princeton Instruments, Siemens, Edinburg Instruments, Cevonik Instruments, Newport, Coherent, Stichting Jonh van Geuns Fonds.

For more detail concerning the event have a look onto the web site: http://www.hrsmc.nl/schoolEPA08_programme.html. Thomas Härtling

Thomas Härtling is a PhD student at Technische Universität Dresden, Germany. His PhD project deals with the photochemical manipulation of optical properties of metal nanostructures.

Elisabeta Cecilia Vidami Negoescu is a PhD student at Vrije University in Amsterdam, Dpt. Analytical Chemistry and Applied Spectroscopy. Her research interests centre around the visualization of cytochrome P450 BM3 by surface enhanced resonance Raman spectroscopy.

Linh Tran is a postdoctoral research fellow at the Institute for Nanoscale Physics and Chemistry at the Katholieke Universiteit Leuven. Currently, one of her research projects includes investigating individual silver nanowires and creating 'hot spots' on them with wide-field laser illumination.

Viruthachalam Thiagarajan is a postdoctoral researcher at Commissariat à l'ènergie atomique (CEA), Centre de Saclay, France. His research interests span several areas within fluorescence sensing and ultrafast processes.

CONFERENCE REPORTS

5th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications SPEA5 October 4-8, 2008, Mondello, Sicily.

The fifth edition of the “European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications” was held in Mondello, close to Palermo, Sicily, from October 4 to 8, 2008. As in the 4th meeting, some 200 participants were present, but it seemed to us that more countries were represented in 2008. The large participation (55%) of colleagues from Mediterranean countries (8) is almost traditional, but the Meeting registered for the first time a large number of scientists (19%) from East-European countries (9). Scientists from 14 countries outside Europe, with a particular high participation of Japanese colleagues, confirmed the worldwide effort to implement photocatalytic processes and solar photochemistry as a tool for environmental remediation.

The Meeting was divided into 5 sections:

1. Catalysts and Processes for Solar Light Utilization,
with 1 plenary lecture
K. Kisch, Erlangen, Germany, “Semiconductor Photocatalysis for Novel Organic Syntheses?”
and 7 oral presentations and 25 posters.
2. Photodegradation in Gas and Liquid Systems: Catalysts, Reaction Mechanisms and Processes,
with 1 plenary lecture
C. Minero, Torino, Italy, “Surface Tuning of Reactivity and Selectivity in Photocatalysis”
and 9 oral presentations and 43 posters.
3. Photocatalysts Developments: Preparation, Doping and Characterization,
with 1 plenary lecture
M. Anpo, Osaka, Japan, “New Trends in the Nanoscience and Nanotechnology of Titanium Oxide-based Photocatalysts as Environmental-friendly Catalysts”
and 12 oral presentations and 66 posters.
4. Novel Photocatalytic Processes and Process Assessment,
with 1 plenary lecture
O.M. Alfano, Santa Fé, Argentina, “Modeling of Homogeneous and Heterogeneous Photoreactors: Three Applications to Advanced Oxidation Processes”
and 12 oral presentations and 24 posters.
5. Photocatalysis: from Fundamentals to Applications,
with 7 oral presentations and 26 posters.

The vast majority of scientific contributions was devoted to the preparation and test of new photocatalysts and photocatalyst dopings and to a refined physical description of new catalyst materials. The results reflect the considerable efforts of a large number of research groups to understand in detail the mechanisms of the photocatalytic process and the particular effect of the dopings applied. However, as the vast collection of data

concerning TiO₂ photocatalysis is still increasing, the impression of “remakes” should be avoided by clearly stating the purpose of the work presented. It reflects the high standards of these series of Meetings, that some contributions led to open critical discussions for lack of clear aims and bibliographic knowledge, not adapted analytical procedures and wrong definitions.

Working in many cases with special and unique materials as potential catalysts, the need of standardized procedures and comparable experimental methods was again clearly stated. Extrapolating the tendency reflected by the contributions of the last two Meetings, it may be expected that in the future more lecture time and poster space will be devoted to concepts and the implementation of standardized procedures.

Another critical point addressed at this Meeting concerned applicability. Although, research projects are many times justified with the urgent need to develop processes for efficient environmental remediation, the design of the projects and the corresponding results are rarely evaluated in terms of efficiency, scalability, energy balance, investment and maintenance costs. It is somehow surprising that after more than 30 years of intensive research work in the domain of photocatalysis, only relatively few attempts of technical applications were reported.

Promising ideas also surfaced at this Meeting in an international audience and might initiate some new domains of research and development:

- Techniques and reactions systems enhancing the efficiency of photocatalytic degradation of organic pollutants in aqueous solutions and suspensions. Some W, Mo or V oxide containing catalysts seem to exhibit higher quantum efficiencies of pollutant oxidation than pure or doped TiO₂.
- Photocatalysis for preparative purposes as a tool of Green Chemistry. The plenary lecture of H. Kisch, Erlangen, and the posters of Albini's and Caronna's groups gave a very good picture of the state of the art. In addition, new catalysts were reported that might be used for selective photocatalyzed oxidation reactions.
- Analytic techniques did not appear as a special topic, but interesting contributions dealt with the effect of the photocatalytic oxidation on microorganisms and with the idea of using molecular imprints to evaluate efficiencies of pollutant oxidation in complex waste water matrices.

The meeting provided again an excellent platform to evaluate the state of research and development in the domain of photocatalysis and, to a lesser extent, of solar applications, and to discuss with many colleagues new ideas that might emerge from their results.

The perfect organisation of the Meeting by V. Augugliaro and L. Palmisano and their many helpers falls into a long standing tradition of great Sicilian hospitality enhancing the communication between colleagues of so many different countries and backgrounds. The infrastructure of the Meeting worked to its perfection, and the organizers went as far as to provide for sunny and warm weather at blue but sometimes choppy seas. Also many thanks to the organizers for giving the participants a chance to visit the many beautiful sites of Palermo and, of course, Monreale.



The Participants of the 5th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications. SPEA5.

We are looking forward to a next successful meeting to be held in 2010 in Prague. Although, administrative constraints demand that more and more participants would need to be accepted with an oral presentation, this tendency is contraproductive for the discussion of the results presented and of new ideas emerging, and, hence, for the success of the Meeting. We would propose to establish a program with less oral presentations but more time for discussion of what has been presented as well as of what is shown in the poster sessions.

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CONFERENCE REPORTS

Spring Session of the French Group of Photochemistry (GFP) May 21st – 23rd, 2008, Brest, France.

The 2008 GFP spring meeting took place in the very modern Ecole TELECOM Bretagne, a "prestigious graduate engineering school and international research centre in the field of information technologies", located in the western outskirts of Brest. It was organised by Edmond Amouyal (Ecole Polytechnique, Palaiseau) and Christiane Carré (Optics Department of TELECOM Bretagne, Brest) helped locally by Sylvie Grégoire and Anne Catherine Cariou.

The GFP meeting is an important biannual event giving French photochemists the opportunity to meet and discuss under very relaxed conditions and this year event was not an exception, with 55 participants representing all major photochemistry laboratories in France. Among the 23 talks, many dealt with material sciences, the development of new photoactive molecules and materials, which was not surprising in view of the research activity at Telecom Bretagne. Bio-applications, imaging, environmental topics as well as pure photochemistry were also well represented.

The meeting was opened by Edmond Amouyal (Palaiseau), President of the French Photochemistry Group (GFP), followed by Mr Godefroy Dang Nguyen, Deputy Dean for Research at TELECOM Bretagne, who gave a general presentation of the TELECOM Bretagne graduate school.

The opening talk at the first session was held by Fabrice Odobel (Nantes) who discussed photovoltaic cells. Much effort has been dedicated over the years to improving the Grätzel-type cells, but the efficiency remains limited to about 10 %. In this talk alternative solutions were presented, for example electrolyte-free ones or such with p-type semiconductor electrodes. The use of new dye molecules was also evoked, for example porphyrins or perylene. In view of the ever increasing price of oil, this is indeed an important field for photochemistry. Bénédicte Mailhot (Clermont-Ferrand) gave a talk about the photooxidation of polyethyleneoxide and the how this is related to structural changes and Emanuela Berni (PhD student, Bordeaux) described new photoluminescent probes based on modified $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes. Céline Frochot (Nancy) gave a much appreciated talk about the current strategy in Photodynamic Therapy. She discussed means to increase the selectivity by using various vectors, for example nanoparticles, and how it may be more advantageous to focus on the indirect effect, attacking the new blood-vessels around the tumour rather than the tumour itself. Anne-Claire Robin (Rennes) ended the afternoon session with a talk about "nano-triggers" used to photo-initiate enzymatic reactions such as NO-synthase.

Thursday started with Sylvie Lacombe (Pau) giving a talk about mesoporous photoactive films that can be used for depollution or disinfection by photooxidation. These are Periodically Organised Mesoporous Thin Films (POMTFs) containing photosensitizing dye molecules. Mohamed Sarakha (Clermont-Ferrand) continued with a talk about the photochemical degradation of an organophosphoric pesticide, azinphos. Olga Tarzi (postdoc, Mulhouse) gave a presentation about the possible use of pyrromethene derivatives as photoinitiators in free radical photopolymerization. She displayed very nice real time FT IR data. Guillaume Sevez (Bordeaux) received a lot of attention for his highly "colored" talk about an 8-state bi-chromophoric system

and its potential use in photo-commuting molecular systems. The session finished with Arnaud Spangenberg (PhD student, Cachan) giving a talk also on photo-commuting systems base on Au nanoparticles.

A poster session was organised during Wednesday afternoon starting with “flash” presentations of posters by Cédric Rouxel (Rennes), Jean-Pierre Malval (Mulhouse), Raymond Chevallier (Brest), Pierre Sévillano (Brest) and Patrice Jacques (Mulhouse). This procedure was very instructive and generated a lot of interest and questions for the posters which was highly appreciated. The posters were then on display during the whole of the conference.

The afternoon special session was dedicated to Optical Materials and started with Isabelle Ledoux (Cachan) giving an invited and nice lecture on photo-commutable systems for non-linear optics. Jean-Luc Fillaut (Rennes) continued with a talk on non-linear optical properties of ruthenium based organometallic nanocomposites. Elena Ishow (Cachan) described new photoactive materials aimed for optical storage, showing examples of structural changes, for example surface gratings, induced by UV light. Carole Arnaud (PhD student, Palaiseau) gave a detailed description of light induced phase transitions in polymeric nanoparticles. Dominique Bosc (Lannion) discussed photoinduced changes in refraction indices and how such materials can be useful in ultrafast telecommunications. He asked photochemists in general to provide new molecules with large response > 300 nm. Alexey Denisov (PhD student, Brest) continued with a talk on the enhancement of the photorefractive effect in polymer-liquid crystal composite materials. The afternoon session was rounded off by Denis Battarel from HOLOTETRIX, Brest, who gave a talk entitled "Diffusion des micro-optiques dans l'industrie". HOLOTETRIX's is a spin-off company of the TELECOM Bretagne Optics Department and its primary activities are the design, fabrication and commercialization of prototype diffractive optical elements (DOE) and micro-optics for diverse industrial applications.

After the end of the Thursday scientific session, a bus ride to the centre and historic port of Brest was organised, where the participants could stroll around in a very sunny (!) weather.

The day finished with a conference dinner which was held in one of the restaurant halls at TELECOM Bretagne. With a nice view of the coast-line the dinner was accompanied by genuine celtic music performed by Damien Malardé and Nolwenn Dissaux, both students at TELECOM Bretagne, as well by Christiane Carré's young son and daughter. The fragile sound of the Celtic harp contrasted a lot with the aural attack of the “bombarde”, a deceivingly small clarinet.

The Friday session started with a talk by Damien Malardé (PhD student, Brest) about the development of a new compact refractometer with ultra-high precision (10^{-6}) for measuring the salt level in the oceans. Olivier Soppera (Mulhouse) continued with a talk on near-field nanopolymerisation using the plasmon resonances in the vicinity of nanoparticles. Julien Gaume (Clermont-Ferrand) presented new results on lithographic gratings obtained by the combined use of photopolymers and liquid crystals. Ruri Hidema (PhD student, Cachan) presented a new family of fluorescent crystals, based on tetrazines. Stéphane Aloïse (Villeneuve d'Asc) presented a very fine photophysical study of various photochromic molecules which triggered off an animated discussion around fundamental photochemical questions. Jean-Pierre Malval (Mulhouse) finished the afternoon session, and the meeting, with a talk on two-photon absorption and polymerization ability of intramolecular energy transfer based photoinitiating systems.

After this last scientific presentation, Jean-Louis De Bougrenet de la Tocnaye, head of the Optics Department and the CNRS FOTON Laboratory at Telecom Bretagne, underlined how

constructive the presence of the Christiane Carré team is in the TELECOM Bretagne Engineering School.

Edmond Amouyal closed the meeting by thanking the local organizers and announcing that the Autumn Meeting of GFP will be held at Ecole Polytechnique in Palaiseau towards the end of November 2008.

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INVITATIONS

XXIV International Conference on Photochemistry July 19th to 24th, 2009, Toledo, Spain

Dear Colleague:

On behalf of the organizing committee, I am pleased to invite you to participate in the upcoming XXIV 24th International Conference on Photochemistry, ICP09, which will be held in Toledo (Spain) from the 19th to the 24th of July 2009. Website: <http://www.icp09-toledo.com/>

The ICP09 will bring together scientists and engineers (around 600 participants) from around the world to discuss the most recent developments in several fields of science and technology using light to interrogate and control matter. The Conference will consist of: 9 plenary lectures, more than 35 invited lectures and over 100 oral contributions, including 3 parallel lecture sessions and 4 poster sessions.

The conference will cover the following topics: Photonics and Imaging / Photochromic Materials and Molecular Switches / Art Conservation / Single Molecule Spectroscopy / Photoinduced Electron and Charge Transfer / Femto(bio)chemistry / Intense Laser Fields / Photo- and Stereochemistry / Photochemistry in Confined Media / Quantum Dots and Nanophotonics / Photocatalysis / H-Bonding and Solvation Dynamics / Theoretical Photochemistry / Applied Photochemistry / Basic Photochemical Processes / Environmental and Atmospheric Photochemistry / Singlet Oxygen in Chemistry, Biology and Medicine / Polymer Photochemistry / Energy Transfer / Photovoltaic Materials and Processes / Structural Dynamics / Coherent Control / Photoactive Biomolecules / Spectroscopic Methods and Application.

A Keynote/Opening lecture will be delivered by A. H. Zewail (USA). Plenary Lectures will be delivered by: M. Chergui (Switzerland), G. R. Fleming (USA), J.T. Hynes (France/USA), A. Griesbeck (Germany), J. Manz (Germany), H. Miyasaka (Japan), M. Orrit (Netherlands), and V. Sundström (Sweden).

For the Invited Lectures, the following scientists have already confirmed their participation: M. Roeffaers (Belgium), M. Sauer (Germany), E. Vauthey (Switzerland), F. Scandola (Italy), P. Plaza (France), D. Zhong (USA), A. Zehnacker (France), M. Olivucci (Italy), H. Masuhara (Japan), H. Garcia (Spain), J. Waluk (Poland), K. Bhattacharyya (India), V. Ramamurthy (USA), J. Moser (Switzerland), R. Pansu (France), S. Costa (Portugal), K. Ghiggino (Australia), M. A. Sabry (Egypt), S. Nonell (Spain), F. Brouwer (Netherlands), D. Kim (Korea), H. Gong (China), A. Rubio (Spain), T. Elsaesser (Germany), H. Petek (USA), M. Dantus (USA), S. Monti (Italy), M-E. Zadeh (Spain).

More information about the meeting can be found on the website <http://www.icp09-toledo.com/>

First circular:

http://www.icp09-toledo.com/cont/first_cir.html

Second circular: To obtain the second circular, please pre-register at the conference website at <http://www.icp09-toledo.com>. The second circular (beginning of 2009) will contain the final program, registration forms and travel details, information on accommodation and social events. . Please note that the pre-registration is NOT the final registration to the conference. It allows getting the second circular to proceed for the final registration including payment of the related fees.

The companies and institutions interested in sponsoring and/or exhibiting their products, can find the procedure on the website of the meeting (Invitation to sponsors and exhibitors) or directly at:

http://www.icp09-toledo.com/cont/inv_spon.html

For the pre-registration, visit:

<http://www.icp09-toledo.com/cont/pre-reg.html>

I am looking forward to welcoming you in Toledo (Spain).

Best wishes,

Abderrazzak Douhal

Chairman of the ICP09, Toledo, Spain.

e-mail: conference.icp2009@uclm.es

Following an agreement with the organizers of the International Conference on Photochemistry 2009, EPA members will pay reduced registration fees

MEMBERSHIP APPLICATION FORM



EUROPEAN PHOTOCHEMISTRY ASSOCIATION 2009 MEMBERSHIP RENEWAL/APPLICATION FORM

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

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

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