

General information about the European  
Photochemistry Association

is available at:

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

**Newsletter Editor: Dr. David WORRALL**

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

© 2009 Department of Chemistry, Loughborough University

ISSN 1011-4246

Printed in the United Kingdom by Media Services, Loughborough  
University, Leicestershire LE11 3TU

*CONTENTS*

<b>EPA EXECUTIVE COMMITTEE</b>	<b>4</b>
<b>EDITORIAL</b>	<b>7</b>
President's Letter	7
<b>MINUTES OF THE EPA GENERAL ASSEMBLY</b>	<b>8</b>
<b>THE STATUTES OF THE EUROPEAN PHOTOCHEMISTRY ASSOCIATION</b>	<b>11</b>
<b>EPA PHD PRIZE</b>	<b>17</b>
EPA prize for PhD Thesis on Photochemistry	17
<b>THE HAMMOND MEDAL</b>	<b>18</b>
<b>GRAMMATICAS-NEUMANN PRIZE 2010</b>	<b>19</b>
<b>ACTIVITIES OF NATIONAL GROUPS</b>	<b>20</b>
Photochemistry in the Czech Republic	20
<b>TECHNICAL REPORT</b>	<b>37</b>
Solvatochromism of thioxanthone (TX) in the light of CAS PT2 computations	37
<b>PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES</b>	<b>54</b>
<b>PUBLICATIONS</b>	<b>55</b>
Abstracts of Theses in Photochemistry	55
Andrew McKinley	55
Angela E. Raabe	57

Pavel Müller	59
Arnulf Rosspeintner	61
Giacomo Bergamini	61
Yong Sheng Zhao	71
Zsombor Miskolczy	75
Fadi Hatoum	77
Peter Zoon	78
Celia Paris	80
Izabela Franssen	82
Hubert Piwoński	84
Natalia Urbańska	85
Books	87
Review: Photochemistry of Organic Compounds: From Concepts to Practice	87
<b>CONFERENCE REPORTS</b>	<b>89</b>
XXII IUPAC Symposium on Photochemistry July 28– August 1, 2008, Gothenburg, Sweden	89
HRSMC Summer School "Photochemistry 2008: Fundamentals and Applications" May 31 – June 4 2008, Castle Vaeshartelt, Maastricht, The Netherlands	92
5th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications SPEA5 October 4-8, 2008, Mondello, Sicily.	95
Spring Session of the French Group of Photochemistry (GFP) May 21 <sup>st</sup> – 23 <sup>rd</sup> , 2008, Brest, France.	99
Report on the Autumn Meeting of the French Group of Photochemistry	103
The 40 <sup>th</sup> anniversary of the French Group of Photochemistry (GFP)	108
<b>INVITATIONS</b>	<b>112</b>
XXIV International Conference on Photochemistry July 19 <sup>th</sup> to 24 <sup>th</sup> , 2009, Toledo, Spain	112
France Italy Symposium on Photosciences	115
Light in Life Sciences Conference 2009	116
Molecular Science for Solar Fuel	118

EPA Newsletter	3	June 2009
Light in Life Sciences 2009		119
Central European Conference on Photochemistry CECP 2010		121
6th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA6)		122
<b>MEMBERSHIP APPLICATION FORM</b>		<b>123</b>

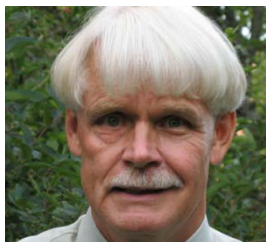
## EPA EXECUTIVE COMMITTEE

---



### President

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



### Vice-President

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



### Treasurer

Dr. Silvio Canonica  
EAWAG  
Ueberlandstrasse 133  
CH-8600 Duebendorf  
Switzerland  
Tel: +41 44 823 54 53  
Fax: +41 44 823 52 10  
Email: [canonica@eawag.ch](mailto:canonica@eawag.ch)



### **Membership**

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



### **Public Relations**

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



### **Past President**

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

**Responsible for PPS matters:**

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

**Newsletter Editor:**

Dr. David Worrall  
Photochemistry Research Group  
Department of Chemistry  
Loughborough University  
Leicestershire LE11 3TU, UK  
Tel: +44(0)1509 222567  
Fax: +44(0)1509 223925  
Email: d.r.worrall@lboro.ac.uk  
Web: <http://www.lboro.ac.uk/departments/cm/staff/worrall.html>

**Website manager:**

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



## EDITORIAL

---

### President's Letter

After the electronic version of our Newsletter at the end of last year, this year it is again a printed booklet thanks to the efforts of David Worrall. We intend to continue to produce one electronic and one printed issue of the Newsletter including all important information from the past twelve months. For example, you will find here the new statutes of the EPA approved at our General Assembly held July 30<sup>th</sup>, 2008 (page 11).

Continuing our series of highlighting photochemistry activities in various European countries, this Newsletter focuses on the Czech Republic. A series of articles, coordinated by Petr Klán, reveals the multiple directions of the research conducted by ten groups covering various aspects of the interaction of light with molecular systems.

The current research activity in our field, all over Europe and beyond, is also reflected in the numerous abstracts of PhD thesis published here. Now is a good time to remind you that the second Prize for the best PhD thesis in the field of Photochemistry will be presented in 2010, with the deadline for nominations at the end of this year (Page 17). Young scientists will not be the only recipients of an EPA Prize. I am pleased to announce that EPA has created an award for the most cited communication or articles published in *Photochemical & Photobiological Sciences*, the journal jointly owned by the EPA. The corresponding author will receive 1000 €, and to qualify must be an EPA member. The first award will be presented in 2010 and will consider publications appeared in the previous three years. We therefore encourage our members to publish their best work in *Photochemical & Photobiological Sciences* to qualify for this award.

I am also pleased to inform you that *Photochemical & Photobiological Sciences* is sponsoring the plenary lecture to be given by Michel Orrit at the International Conference on Photochemistry in Toledo (page 112). The Toledo conference will be the next important appointment for our community and I look forward to seeing many of our members at this meeting.

Dimitra Markovitsi  
EPA President

## 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 30<sup>th</sup>, 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-KNOWLEDGE**, 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 an account to which EPA members pay their dues and where other official revenues and expenses are recorded.

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

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

## **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@unige.ch](mailto:eric.vauthey@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:**

**William Jenks (USA)**  
Department of  
Chemistry  
Iowa State University  
1605 Gilman Hall  
Ames, IA 50011-3111  
[wsjenks@iastate.edu](mailto:wsjenks@iastate.edu)

## **Grammaticas-Neumann Prize 2010**

---

### **Call for Nominations**

The Photochemistry Section of the Swiss Chemical Society (which acts as the Swiss section of the European Photochemistry Association, EPA) is pleased to invite nominations for the international Grammaticakis-Neumann Prize 2010. The Prize consists of a diploma and a financial award of 5'000 Swiss Francs (for each awardee, if there is more than one), and it is presented once a year to a young research scientist (<40 at the time when he or she receives the prize) from academia or from industry for outstanding contributions to the science of photochemistry. The Prize, for which nominations are now being invited, will be presented during the 2010 Fall Meeting of the Swiss Chemical Society. The award ceremony will be followed by a lecture of the laureate which is also to be published in the official EPA journal, *Photochemical and Photobiological Sciences*.

Each member of the EPA, or one of its sister organizations (such as the Inter-American Photochemical Society) can nominate an individual as candidate for the Grammaticakis-Neumann Prize. Such nominations, accompanied by supporting documentation (detailed justification, curriculum vitae, list of publications, and at least two supporting letters), should be submitted by e-mail (with attachments) to the executive director of the Swiss Chemical Society, Dr. Lukas Weber ([weber@scg.ch](mailto:weber@scg.ch)). The closing date for nominations is October 10, 2009 (see also

[www.scg.ch/awards/grammaticakis.html](http://www.scg.ch/awards/grammaticakis.html)).

Previous laureates of the Grammaticakis-Neumann Prize are Alexander Heckel (2008), Alberto Credi (2007), Torsten Fiebig and Achim Wagenknecht (2006), Dario Bassani (2005), Johan Hofkens (2003), Nicola Armaroli (2001), Dirk Guldi (2000), Werner Nau and Eric Vauthey (1999), Axel Griesbeck (1997), Matthew Zimmt (1996), Luisa de Cola (1995), Pedro Aramendia (1994), Mark van der Auweraer (1992), V. Ramamurthy (1991), Wolfgang Rettig (1990), Martin Demuth (1987), Ian Gould and Anthony Harriman (1985).

In other years (e.g. in 2009) no prize was awarded, because no suitable candidate was proposed.

## ACTIVITIES OF NATIONAL GROUPS

---

### Photochemistry in the Czech Republic

The following is a summary of key activities in the field of photochemistry, photophysics and, to some extent, photobiology in the Czech Republic. Ten research groups present brief overviews of their current scientific programs and the most important achievements. The list, sorted alphabetically according to the program titles, has been compiled based on the information kindly provided by the research coordinators and is probably not fully comprehensive. It should also be noted here that a distinguished American photochemist of Czech origin, Josef Michl, has newly established a research group at the Institute of Organic Chemistry and Biochemistry in Prague.

Petr Klán

### Microwave Chemistry, Photochemistry and Technology

*Research coordinators:* Vladimír Církva ([cirkva@icpf.cas.cz](mailto:cirkva@icpf.cas.cz)); Milan Hájek ([hajek@icpf.cas.cz](mailto:hajek@icpf.cas.cz)); Stanislav Relich ([relich@icpf.cas.cz](mailto:relich@icpf.cas.cz)); Jiří Sobek ([sobek@icpf.cas.cz](mailto:sobek@icpf.cas.cz))

*Address:* Environmental Process Engineering Laboratory, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague, Czech Republic

*URL:* <http://home.icpf.cas.cz/cirkva/Eng/index.htm>

The research group is engaged in investigations in an interdisciplinary field involving both photochemistry and microwave chemistry, called microwave photochemistry [1], describing chemical reactions initiated under non-classical conditions. The objective of the research program is to study a combination effect of two distinctive kinds of electromagnetic radiation, UV/Vis and microwave, on chemical and physical properties of the molecules.

The scope of the microwave photochemistry is mostly, but not essentially, connected with the electrodeless discharge lamp (EDL) which generates UV/Vis radiation when placed in the microwave field [2]. The lamp consists of a glass (Pyrex, quartz) tube filled under a lower pressure with argon and an excitable substance, such as mercury or sulfur. An experimental vacuum system for the EDL manufacture [3] has been recently designed by us. The technique is very simple and enables the EDL preparation in a conventional chemistry laboratory. In addition, the EDL has been coated with the TiO<sub>2</sub> thin film as an efficient photocatalyst.

EDLs with the suitable operating parameters (argon pressure, solution temperature, and solvent polarity) and spectral characteristics have been applied for selected photochemical (dimerization of 2- and 4-*tert*-butylphenols; *E-Z* photoisomerization of stilbene and cinnamic acid derivatives; photocyclization to the phenanthrene derivatives) [4] and photocatalytic (degradation of monochloroacetic acid; Rhodamine B) [5] reactions.

*Representative publications*

1. Klán P., Církva V., *Microwaves in Photochemistry*, in *Microwaves in Organic Synthesis*, ed. by Loupy A. Wiley/VCH, Weinheim, 2006, pp 860-897.
2. Müller P., Klán P., Církva V., The Electrodeless Discharge Lamp: A Prospective Tool for Photochemistry. Part 4. Temperature- and Envelope Material-Dependent Emission Characteristics. *J. Photochem. Photobiol. A* 2003, 158, 1-5.
3. Církva V., Vlková L., Relich S., Hájek M., Microwave Photochemistry IV: Preparation of the Electrodeless Discharge Lamps for Photochemical Applications. *J. Photochem. Photobiol. A* 2006, 179, 229-233.
4. Církva V., Kurfürstová J., Karban J., Hájek M., Microwave Photochemistry III: Photochemistry of 4-*tert*-Butylphenol. *J. Photochem. Photobiol. A* 2005, 174, 38-44.
5. Církva V., Žabová H., Hájek M., Microwave Photocatalysis of Monochloroacetic Acid over Nanoporous Titanium (IV) Oxide Thin Films using Mercury Electrodeless Discharge Lamps. *J. Photochem. Photobiol. A* 2008, 198, 13-17.

## Organometallic Photophysics

*Research coordinators:* Stanislav Zálisř ([zalis@jh-inst.cas.cz](mailto:zalis@jh-inst.cas.cz)); Antonín Vlček (jointly with Queen Mary, University of London; [a.vlcek@qmul.ac.uk](mailto:a.vlcek@qmul.ac.uk)); Martin Hof ([martin.hof@jh-inst.cas.cz](mailto:martin.hof@jh-inst.cas.cz)); Jan Sýkora ([jan.sykora@jh-inst.cas.cz](mailto:jan.sykora@jh-inst.cas.cz))

*Address:* J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague, Czech Republic

URL: <http://www.chem.qmul.ac.uk/staff/vlcek/index.html>

Our research strives to understand the nature, dynamics, relaxation and reactivity of electronically excited transition-metal compounds and provide enabling knowledge for the development of new photoactive metal complexes applicable in molecular devices or solar energy conversion. We carry out combined theoretical and experimental investigations of charge transfer excited states of various transition metal organometallic chromophores, presently concentrating on  $\text{Re}^{\text{I}}$  carbonyl-diimines,  $[\text{Re}(\text{L})(\text{CO})_3(\text{N},\text{N})]^n$  ( $\text{N},\text{N} = \alpha$ -diimine). These are chemically robust and synthetically flexible photo- and redox active compounds, which can be incorporated into supramolecular systems, polymers or biomolecules.  $\text{Re}^{\text{I}}$  complexes are efficient and fast photosensitizers triggering electron- or energy transfer, as well as dynamical structural changes in their molecular environments. We employ DFT and TD-DFT calculations to characterize singlet and triplet excited states by their energies, structural parameters and, most informatively, redistribution of electron density upon excitation. Theoretical results are validated by comparing calculated and experimental stationary as well as time-resolved UV-Vis, luminescence, IR and resonance Raman spectra. Quantum chemical calculations are indispensable for understanding ultrafast excited-state dynamics; that is evolution of the molecular system from the instant of photon absorption until formation of a stable photoproduct or ground-state recovery. Moreover, they challenge and change long-established textbook views of excited states: It turns out that regions of excited electron density are delocalized over several ligands [1]. Excited states usually called MLCT (metal to ligand charge transfer) actually involve shifts of



electron density from one part of the molecule, including the metal atom, to an electron-accepting ligand; in the case of  $\text{Re}^{\text{I}}$  complexes they are better viewed as  $\text{Re}(\text{L})(\text{CO})_3 \rightarrow \text{N}, \text{N}$  transitions [1]. Moreover an extensive mixing between CT and intraligand  $\pi\pi^*$  excitation occurs in low-lying triplet states with profound photophysical consequences [2]. Metal-centered dd transitions in substituted heavy-metal carbonyls were found to occur at much higher energies than commonly believed, playing almost no role in the spectroscopy of low-lying excited states [3], although they are important in photochemistry. On the methodological side, it should be noted that results of DFT/TD-DFT excited-state calculations depend sensitively on the choice of various parameters, most importantly the functional and, for CT states, the solvent description.

This is a multidisciplinary research, which involves also Queen Mary, University of London together with the Rutherford Appleton Laboratory (A. Vlček) and the COST D35 Action. Out of recent scientific results, we can highlight the first determination of rates and mechanism of intersystem crossing in Re chromophores [2], the first direct observation and identification of a  $\text{M} \rightarrow \text{CO}$  charge transfer excited state [3], understanding the CO photodissociation mechanism in  $[\text{Ru}(\text{X})_2(\text{CO})_2(\text{N}, \text{N})]$  [1], revealing the reasons for unusually fast (ps) decay of MLCT excited states of metal nitropolypyridine complexes [1], identification of picosecond-lived ligand-to-ligand CT excited states in  $\text{Re}^{\text{I}}$  carbonyl-diimine complexes with electron-rich amido- or phosphido ligands [4], and establishing  $\text{Re}^{\text{I}}$  complexes as IR probes of medium (solvation) dynamics in ionic liquids [5] or proteins. Currently, we are extending this research into photoinduced electron transfer in supramolecular assemblies and biomolecules, using  $\text{Re}^{\text{I}}$  complexes as excited-state electron acceptors. In particular, we are searching for mechanisms whereby electron transfer can be accelerated into femto-picosecond time domain by specific interactions of the excited chromophore and/or by coupling with structural motions and fluctuations.

*Representative publications*

1. Vlček A., Jr.; Zálíš S., Modeling of Charge Transfer Transitions and Excited States in d6 Transition Metal Complexes by DFT Techniques, *Coord. Chem. Rev.* 2007, 251, 258-287.
2. Cannizzo A.; Blanco-Rodríguez A. M.; Nahhas A.; Šebera J.; Zálíš S.; Vlček A., Jr.; Chergui M., Femtosecond Fluorescence

- and Intersystem Crossing in Rhenium(I) Carbonyl-Bipyridine Complexes, *J. Am. Chem. Soc.* 2008, 130, 8967-8974.
3. Zálíš S.; Farrell I. R.; Vlček A., Jr., The Involvement of Metal-to-CO Charge Transfer and Ligand-Field Excited States in the Spectroscopy and Photochemistry of Mixed-Ligand Metal Carbonyls. A Theoretical and Spectroscopic Study of  $[\text{W}(\text{CO})_4(1,2\text{-ethylenediamine})]$  and  $[\text{W}(\text{CO})_4(\text{N},\text{N}'\text{-bis-Alkyl-1,4-diazabutadiene})]$ , *J. Am. Chem. Soc.* 2003, 125, 4580-4592.
  4. Gabrielsson A.; Busby M.; Matousek P.; Towrie M.; Hevia E.; Cuesta L.; Perez J.; Zálíš S.; Vlček A., Jr., Electronic Structure and Excited States of Rhenium(I) Amido and Phosphido Carbonyl - Bipyridine Complexes Studied by Picosecond Time-Resolved IR Spectroscopy and DFT Calculations., *Inorg. Chem.* 2006, 45, 9789-9797.
  5. Blanco-Rodríguez A. M.; Ronayne K. L.; Zálíš S.; Sýkora J.; Hof M.; Vlček A., Jr., Solvation-Driven Excited-State Dynamics of  $[\text{Re}(4\text{-Et-pyridine})(\text{CO})_3(2,2'\text{-bipyridine})]^+$  in Imidazolium Ionic Liquids. A Time-Resolved Infrared and Phosphorescence Study, *J. Phys. Chem. A* 2008, 112, 3506-3514.

### Photobiophysics in Laboratory of Biophysics

Research coordinators: Jan Naus ([naus@prfnw.upol.cz](mailto:naus@prfnw.upol.cz)); Petr Ilík ([ilik@prfnw.upol.cz](mailto:ilik@prfnw.upol.cz)); Dušan Lazár ([lazard@seznam.cz](mailto:lazard@seznam.cz)); Pavel Pospíšil ([pospip@prfnw.upol.cz](mailto:pospip@prfnw.upol.cz)); Martina Špundová; Pavel Krchňák; Vladimíra Hlaváčková; Iva Šnyrychová; Petr Sušila; Jiří Jablonský

Address: Laboratory of Biophysics, Department of Experimental Physics, Faculty of Science, Palacký University, tř. Svobody 26, 771 46 Olomouc, Czech Republic

URL: <http://exfyz.upol.cz/bf/en/index.htm>

The experimental part of our research is focused on biophysical processes in plants, especially those related to light reactions of photosynthesis and responses of plants to stresses, including systemic response and plant signaling [1-3]. The systems we study are very complex and, therefore, it is necessary to use a wide range of

methodological approaches. We employ classical biochemical methods (electrophoresis of pigment-protein complexes, activities of enzymes, analysis of pigment concentrations) as well as methods that enable us to analyze physiological status of plants (rate of CO<sub>2</sub> assimilation, transpiration and O<sub>2</sub> evolution, surface electric potentials of leaves). However, the basic tools, we use, are kinetic and steady-state fluorescence spectroscopy (fluorescence induction, Q<sub>A</sub><sup>-</sup> reoxidation, quenching analysis, fluorescence imaging, fluorescence temperature curve, emission and excitation spectra at room temperature and at 77 K, lifetime measurements), absorption spectroscopy (including optical spectra of leaves), thermoluminescence and electron paramagnetic resonance (EPR). The latter is used namely to study oxidative stress via detection of reactive oxygen species with the help of spin trapping compounds.

The data obtained in experiments are also theoretically simulated, using mathematical models based on physical principles of given phenomena. Using this approach, it is possible to gain deeper insight into the nature of studied processes. We are mainly interested in modeling of signals that reflect the function of electron transport chain during the light reaction of photosynthesis [4-5] and in simulation of optical properties of leaves. One of our aims is also to use advanced statistical methods to detect early changes in physiological parameters of plants exposed to stress.

*Representative publications*

1. Šnyrychová I., Ayaydin F., Hideg É., Detecting Hydrogen Peroxide in Leaves in vivo - A Comparison of Methods, *Physiol. Plant.* 2009, 135, 1-18.
2. Yamashita A., Nijo N., Pospíšil P., Morita N., Takenaka D., Aminaka R., Yamamoto Yo., Yamamoto Ya., Quality Control of Photosystem II: Reactive Oxygen Species Are Responsible for the Damage to Photosystem II under Moderate Heat Stress, *J. Biol. Chem.* 2008, 283, 28380-28391.
3. Hlaváčková V., Nauš J., Chemical Signals as a Rapid Long-Distance Information Messenger after Local Wounding of a Plant? *Plant Signal. Behav.* 2007, 2, 103-105.
4. Jablonský J., Sušila P., Lazár D., Impact of Dimeric Organization of Enzyme and its Function: The Case of Photosynthetic Water Splitting, *Bioinformatics* 2008, 24, 2755-2759.

5. Jablonský J., Lazár D., Evidence for Intermediate S-States as Initial Phase in the Process of Oxygen Evolving Complex Oxidation. *Biophys. J.* 2008, 94, 2725-2736.

### Photocatalytic Materials

*Research coordinators:* Václav Štengl ([stengl@uach.cz](mailto:stengl@uach.cz)); Vendula Houšková ([houskova@uach.cz](mailto:houskova@uach.cz)); Snejana Bakardjieva ([bakardjieva@uach.cz](mailto:bakardjieva@uach.cz)); Nataliya Murafa ([murafa@uach.cz](mailto:murafa@uach.cz))

*Address:* Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Husinec-Řež, Czech Republic

*URL:* <http://www.uach.cz>

Group scientific activities: (a) Preparation of photocatalytic materials based on titania, zinc oxide and doped titania from aqueous solutions by homogeneous hydrolysis methods or from non-aqueous solutions by modified sonochemical sol-gel methods for photochemical applications using visible light. (b) The characterization of UV-photocatalytic powder materials by degradation of Orange 2 dye using a visible spectrophotometry, and of Vis-photocatalytic powder materials by degradation of salicylic acid using a fluorescence spectrophotometry. (c) Testing the photocatalytic layers activity on gas phase acetone, toluene, or benzene degradation efficiency using a mass spectrometry. (d) Preparation and characterization of special photocatalytic materials for water splitting or degradation of warfare agents.

#### *Representative publications*

1. Österlund L., Štengl V., Bakardjieva S., et al., Effect of Sample Preparation and Humidity on the Photodegradation Rate of CEES on Pure and Zn Doped Anatase TiO<sub>2</sub> Nanoparticles Prepared by Homogeneous Hydrolysis, *Appl. Cat., B* 2009, 88, 194-203.
2. Štengl V., Bakardjieva S., Murafa N., Preparation and Photocatalytic Activity of Rare Earth Doped TiO<sub>2</sub> Nanoparticles,

*Mat. Chem. Phys.* 2009, 114, 217-226.

3. Štengl V., Bakardjieva S., Murafa N. et al., Visible-Light Photocatalytic Activity of TiO<sub>2</sub>/ZnS Nanocomposites Prepared by Homogeneous Hydrolysis, *Microporous Mesoporous Mater.* 2008, 110, 370-378.
4. Štengl V., Bakardjieva S., Murafa N., et al., Preparation, Characterization and Photocatalytic Activity of Optically Transparent Titanium Dioxide Particles, *Mat. Chem. Phys.* 2007, 105, 38-46.
5. Bakardjieva S., Štengl V., et al., Photoactivity of Anatase-Rutile TiO<sub>2</sub> Nanocrystalline Mixtures Obtained by Heat Treatment of Homogeneously Precipitated Anatase, *Appl. Cat., B* 2005, 58, 193-202.

### **Photochemistry and Photobiology at the Institute of Physical Biology**

*Research coordinators:* Tomáš Polívka ([polivka@ufb.jcu.cz](mailto:polivka@ufb.jcu.cz)); Marcel Fuciman ([fuciman@greentech.cz](mailto:fuciman@greentech.cz)); Milan Durchan; František Vácha ([vacha@jcu.cz](mailto:vacha@jcu.cz)); Petr Hříbek

*Address:* Institute of Physical Biology, University of South Bohemia, Zámek 136, 37333 Nové Hradky, Czech Republic

*URL:* <http://www.ufb.jcu.cz>

The research is focused on ultrafast excited-state dynamics of various systems, ranging from molecules in organic solvents to large pigment-protein complexes from photosynthetic organisms. The lab is equipped with an amplified femtosecond laser system delivering pulses of ~120 fs duration with energies of 2 mJ/pulse centered at 790 nm. These primary pulses are further utilized to generate excitation and probe pulses in a broad range of wavelength (250-1900 nm) using parametric amplifier(s) and/or white-light continuum. Besides the standard transient absorption technique, we have also

developed pump-dump-probe experimental set-up that utilizes two tunable parametric amplifiers as the sources of pump and dump pulses.

*Carotenoid excited-state dynamics.* The main photochemistry research of the group focuses on excited-state dynamics of carotenoids, especially on the role of dark excited states in relaxation processes. The aim of our current research is to reveal relations between the excited-state dynamics and structure of the particular carotenoid. Influence of various functional groups (e.g. conjugated carbonyl group or conjugated phenolic ring) on energies and lifetimes of excited state is studied by application of transient absorption spectroscopy to a number of carotenoids with various structures and/or functional groups.

*Energy transfer and photoprotection in photosynthesis.* Based on the knowledge gathered from studies of carotenoids in solution, we work on elucidation of carotenoid functions in various carotenoid-binding proteins, ranging from photosynthetic antenna of plants and bacteria to specific carotenoid binding proteins with so far unknown function. Although the main focus is on efficiencies and pathways of energy transfer from carotenoids to (bacterio)chlorophylls in light-harvesting systems, photoprotective role of carotenoids is also studied. Typically, formation of carotenoid radicals that have been related to quenching of (bacterio)chlorophyll excited states is also studied in our group.

*Energy/electron transfer processes in synthetic systems.* Recently we have also started to study ultrafast processes in synthetic systems that aim to work as molecular devices carrying out either energy or electron transfer processes. Studies of carotenoid-pyropheophorbide dyads that can tune energy transfer efficiency by changing solvent polarity showed large potential of these molecules. Besides the carotenoid-based artificial systems, we also study various porphyrin-related molecules, in which electron and energy transfer processes are of high interest.

*Representative publications*

1. Polívka T., Balashov S. P., Chábera P., Imasheva E. S., Yartsev A., Sundström V., Lanyi J. K., Femtosecond Carotenoid to Retinal Energy Transfer in Xanthorhodopsin, *Biophys. J.* 2009, 6, 2268–2277.

2. Polívka T., Pascher T., Hiller R. G., Energy Transfer in the Peridinin-Chlorophyll Protein Complex Reconstituted with Mixed Chlorophyll Sites., *Biophys. J.* 2008, 94, 3198-3207.
3. Polívka T., Niedzwiedzki D., Fuciman M., Sundström V., Frank H. A., Role of B800 in Carotenoid-Bacteriochlorophyll Energy and Electron Transfer in LH2 Complexes from the Purple Bacterium Rhodospirillum rubrum, *J. Phys. Chem. B* 2007, 111, 7422-7431.
4. Polívka T., Pellnor M., Melo E., Pascher T., Sundström V., Osuka A., Naqvi K. R., Polarity-Tuned Energy Transfer Efficiency in Artificial Light-Harvesting Antennae Containing Carbonyl Carotenoids Peridinin and Fucoxanthin, *J. Phys. Chem. C* 2007, 111, 467-476.

### Photochemistry and Photophysics of Organic Compounds

*Research coordinators:* Petr Klán <sup>a</sup> ([klan@sci.muni.cz](mailto:klan@sci.muni.cz)); Dominik Heger <sup>a</sup> ([hegerd@chemi.muni.cz](mailto:hegerd@chemi.muni.cz)); Jana Klánová <sup>b</sup> ([klanova@recetox.muni.cz](mailto:klanova@recetox.muni.cz)); Jaromír Literák <sup>a</sup> ([literak@chemi.muni.cz](mailto:literak@chemi.muni.cz))

*Addresses:* <sup>a</sup> Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5/A8, 625 00 Brno, Czech Republic; <sup>b</sup> RECETOX, Faculty of Science, Masaryk University, Kamenice 3, 625 00 Brno, Czech Republic

URL: <http://www.sci.muni.cz/photochemistry>

The group is engaged in a variety of research projects that deal with mechanistic organic photochemistry, emphasizing the use of photochemistry to solve some interdisciplinary problems in chemistry, physics, and environmental sciences. The research keywords include: Photoremovable protecting groups; Photoactivatable compounds; Kinetic flash photolysis; Organic synthesis using photochemical steps; Energy transfer; Environmental photochemistry; Microwave (electrodeless) discharge lamps. The studies involve a broad spectrum of chemical and physico-chemical methods and applications, such as modern organic synthesis,

structural analysis, or nanosecond and femtosecond kinetic laser flash photolysis. The emphasis is on data processing and, in some cases, on quantum-chemical calculations.

In the past years the photochemical group has developed several new *photoactivatable compounds*, that is, the systems which photochemically release (“uncage”) the molecules of interest in order to use them in biological studies and applied chemistry [1-3]. A great advantage of photochemical activation over other stimuli in such applications is the ability to precisely control the processes in time and space.

Study of the chemical effects resulting from the irradiation of ice or snow field samples or laboratory-produced frozen aqueous solutions with UV light is now an active research area relevant to atmospheric and terrestrial chemical processes taking place in high latitude and altitude environments. The investigations of the research group have recently shown that photochemistry of trace organic compounds of anthropogenic origin in natural ice or snow could become a significant burden to the polar environment [4]. Some laboratory studies have also been focused on understanding the interfacial interactions between ice/snow and organic molecules [5].

*Representative publications*

1. Zabadal M., Pelliccioli A. P., Klán P., Wirz J., 2,5-Dimethylphenacyl Esters: A Photoremovable Protecting Group for Carboxylic Acids, *J. Phys. Chem. A* 2001, 105, 10329-10333.
2. Plíštil L., Šolomek T., Wirz J., Heger, D., Klán P., Photochemistry of 2-Alkoxyethyl-5-methylphenacyl Chloride and Benzoate, *J. Org. Chem.* 2006, 71, 8050-8058.
3. Pelliccioli A. P., Klán P., Zabadal M., Wirz J., Photorelease of HCl from o-Methylphenacyl Chloride Proceeds through the Z-xilylenol, *J. Am. Chem. Soc.* 2001, 123, 7931-7932.
4. Matykiewiczová, N., Klánová J., Klán P., Photochemical Degradation of PCBs in Snow, *Environ. Sci. Technol.* 2007, 41, 8308-8314.
5. Heger D., Jirkovský J., Klán P., Aggregation of Methylene Blue in Frozen Aqueous Solutions Studied by Absorption Spectroscopy, *J. Phys. Chem. A* 2005, 109, 6702-6709.



### Photochemistry in the Laboratory of Laser Chemistry

*Research coordinators:* Josef Pola ([Pola@icpf.cas.cz](mailto:Pola@icpf.cas.cz)); Radek Fajgar

*Address:* Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague, Czech Republic

*URL:* <http://www.icpf.cas.cz/laser/laser.aspx>

Research involves studies of chemical reactions induced by IR and UV laser radiation in the gas, liquid and solid phase. The emphasis is given to elucidation of homogeneous decompositions of organic and organometallic compounds, gas-phase polymerization of laser-generated unstable species, gas-phase and solution-phase chemical deposition of novel materials (polymers, nanosized inorganic compounds, nanometals, nanocomposites), ablation of polymers leading to deposition of novel polymeric films, and degradation of gaseous and liquid-phase pollutants. All these laser-induced reactions have specific features that are not attainable using other energy sources.

#### *Representative publications*

1. Pola J., Kupčik J., Durani S. M. A., Khavaja E. E., Masoudi H. M., Bastl Z., Šubrt J., Laser Ablative Structural Modification of Poly(ethylene-alt-maleic anhydride), *Chem. Mater.* 2003, 15, 3887-3893.
2. Ouchi A., Bastl Z., Boháček J., Orita H., Miyazaki K., Miyashita S., Bezdička P., Pola J., Room-Temperature Interaction between Laser-Chemical Vapour-Deposited Selenium and Some Metals. *Chem. Mater.* 2004, 16, 3439-3445.
3. Pola J., Ouchi A., Bakardjieva S., Urbanová M., Boháček J., Šubrt J., Laser Photolytic Approach to Cu/polymer Sols and Cu/polymer Nanocomposites with Amorphous Cu Phase, *J. Photochem. Photobiol. A* 2007, 192, 84-92.
4. Pola J., Bakardjieva S., Maryško M., Vorlíček V., Šubrt J., Bastl Z., Galíková A., Ouchi A., Laser-Induced Conversion of Silica into Nanosized Carbon- Polyoxocarboasilane Composites, *J. Phys. Chem. C* 2007, 111, 16818-16826.

5. Urbanová M., Pokorná D., Bakardjieva S., Šubrt J., Bastl Z., Pola J., IR Laser-Induced Carbothermal Reduction of Silica, *Eur. J. Inorg. Chem.* 2008, (26), 4111-4116.

### Photochemistry of Free Clusters and Nanoparticles in Molecular Beams

*Research coordinators:* Michal Fárník <sup>a</sup> ([michal.farnik@jh-inst.cas.cz](mailto:michal.farnik@jh-inst.cas.cz)); Viktoriya Poterya <sup>a</sup>; Ondřej Votava <sup>a</sup>; Petr Slaviček <sup>b</sup> ([Petr.Slavicek@vscht.cz](mailto:Petr.Slavicek@vscht.cz))

*Addresses:* <sup>a</sup> Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic; <sup>b</sup> Department of Physical Chemistry, Prague Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic

URL: <http://www.jh-inst.cas.cz/~farnik/>

In 2005 a new unique experiment for studies of free clusters and nanoparticles in molecular beams in vacuum has been set up in the JH Institute of Physical Chemistry. The experiments are complemented by theoretical calculations of a closely collaborating group of P. Slaviček (Prague Institute of Chemical Technology). The research focuses namely in three areas: (1) photochemistry in nanoparticle systems relevant in atmospheric chemistry, (2) photodissociation of small “biomolecules” in cluster environments; and (3) generation and study of novel rare gas molecules.

(1) It includes, e.g., the systems, which play a key role in the ozone depletion process, i.e. hydrogen halide molecules on ice nanoparticles  $\text{HX}\cdot(\text{H}_2\text{O})_n$  ( $\text{X}=\text{Br},\text{Cl}$ ) and pure  $(\text{H}_2\text{O})_n$  clusters. Photodissociation in these systems has been studied; these studies have been extended to nitrogen containing species and at present.

(2) Small heteroaromatic ring molecules, e.g. pyrrole, often act as UV active chromophores in the larger biomolecules and their photochemistry determines the stability of biomolecules. However, solvation can have a profound effect on the photochemistry.

Therefore the photolysis of small heteroaromatic molecules as pyrrole is investigated in cluster environments.

(3) Novel rare gas compounds, e.g., organoxenon molecules H-Xe-CCH, have been generated by photodissociation of molecules (e.g. acetylene) in rare gas clusters. These compounds are extremely interesting from the fundamental point of view since they substantially enrich our understanding of the chemical bonds.

*Representative publications*

1. Poterya V., Fárník M., Slaviček P., Buck U., Kresin V., Photodissociation of Hydrogen Halide Molecules on Free Ice Nanoparticles. *J. Chem. Phys.* 2007, 126, 071101.
2. Ončák M., Slaviček P., Poterya V., Fárník M., Buck U., Emergence of Charge-Transfer-to-Solvent Band in the Absorption Spectra of Hydrogen Halides on Ice Nanoparticles: Spectroscopic Evidence for Acidic Dissociation. *J. Phys. Chem. A* 2008, 122, 5344-5353.
3. Poterya V., Fárník M., Ončák M., Slaviček P., Water Photodissociation in Free Ice Nanoparticles at 243 nm and 193 nm. *Phys. Chem. Chem. Phys.* 2008, 10, 4835-4842.
4. Poterya V., Profant V., Fárník M., Slaviček P., Buck U., Experimental and Theoretical Study of the Pyrrole Cluster Photochemistry: Closing the  $\pi, \sigma^*$  Dissociation Pathway by Complexation. *J. Chem. Phys.* 2007, 127, 064307.
5. Poterya V., Votava O., Fárník M., Ončák M., Slaviček P., Buck U., Friedrich B., Generation and Orientation of Organoxenon Molecule H-Xe-CCH in the Gas Phase. *J. Chem. Phys.* Vol. 2008, 128, 104313.

### **Photodegradation of Organic Pollutants**

*Research coordinator:* Jaromír Jirkovský ([jaromir.jirkovsky@jh-inst.cas.cz](mailto:jaromir.jirkovsky@jh-inst.cas.cz))

*Address:* J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

URL: <http://www.jh-inst.cas.cz>

The subjects of the scientific activity comprise the complex study of photoactive materials based on nanocrystalline titanium dioxide and research of their practical utilization in the field of photocatalytic water and air disinfection, detoxication and total mineralization of organic pollutants.

The research includes (i) synthesis of photoactive nanoparticles of titanium dioxide, (ii) characterization of their physico-chemical properties focused on the relationships between structural parameters and photoactivity, (iii) kinetic and mechanistic studies of the photodegradation of harmful organic substances, (iv) construction of various types of photoreactors for disinfection and purification of polluted water and air as well as (v) development of photoactivity testing methods.

*Representative publications*

1. Heyrovský M., Jirkovský J., Polarography and Voltammetry of Ultrasmall Colloids; Introduction to a New Field, *Langmuir* 1995, 11, 4288-4292.
2. Kolář M., Měšťánková H., Jirkovský J., Heyrovský M., Šubrt J., Some Aspects of Physico-Chemical Properties of TiO<sub>2</sub> Nanocolloids with Respect to Their Age, Size, and Structure, *Langmuir* 2006, 22, 598-604.
3. Macounová K., Krýsová H., Ludvík J., Jirkovský J., Kinetics of Photocatalytic Degradation of Diuron in Aqueous Colloidal Solutions of Q-TiO<sub>2</sub> Particles, *J. Photochem. Photobiol. A: Chem.* 2003, 156, 273-282.
4. Krýsová H., Jirkovský J., Krýsa J., Mailhot G., Bolte M., Comparative Kinetic Study of Atrazine Photodegradation in Aqueous Fe(ClO<sub>4</sub>)<sub>3</sub> Solutions and TiO<sub>2</sub> Suspensions, *Appl. Catal. B: Environ.* 2003, 40, 1-12.
5. Krýsa J., Waldner G., Měšťánková H., Jirkovský J., Grabner G., Photocatalytic Degradation of Model Organic Pollutants on an Immobilized Particulate TiO<sub>2</sub> Layer. Roles of Adsorption Processes and Mechanistic Complexity, *Appl. Catal. B: Environ.* 2006, 64, 290-301.

## Photosensitized Reactions in Supramolecular Systems, Hybrids and Nanostructures

*Research coordinators:* Pavel Kubát <sup>a</sup> ([pavel.kubat@jh-inst.cas.cz](mailto:pavel.kubat@jh-inst.cas.cz)); Kamil Lang <sup>b</sup> ([lang@iic.cas.cz](mailto:lang@iic.cas.cz)); Jiří Mosinger <sup>c</sup> ([mosinger@natur.cuni.cz](mailto:mosinger@natur.cuni.cz))

*Addresses:* <sup>a</sup>J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Praha 8; <sup>b</sup> Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež; <sup>c</sup> Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Praha 2, Czech Republic

*URLs:* <sup>a</sup> <http://www.jh-inst.cas.cz/~kubat>;  
<sup>a</sup> <http://www.iic.cas.cz/~lang>

The cooperation of all three groups lays in chemistry and photophysics of porphyrin-type sensitizers, in the formulation of new photofunctional materials and self-assembled structures with potential impact in medicine, light-harvesting, and sensing. The research focuses on two areas: (1) Photophysics and photochemistry of sensitizers, self-assembled systems and clusters in solution [1-2], and (2) Design, preparation, photophysical characterization, and testing of novel photoactive materials [3-5].

(1) The topic includes the characterization of sensitizers suitable for photodynamic therapy, self-aggregation, the formation of complexes with biologically relevant (DNA, proteins) and transport (cyclodextrins, calixarenes) molecules, the photorelease of gas molecules from clusters and solution-phase self-assemblies. We also study photoinduced electron/energy transfer processes within these systems and the formation and reactivity of singlet oxygen in solutions.

(2) The materials are based on singlet oxygen producing sensitizers intercalated into layered materials (layered silicates, layered double hydroxides) or embedded in polymeric nanofabrics and silica matrices. The topic includes the characterization of photophysical properties in solid matrices (fluorescence, excited states, singlet oxygen). We have found that functionalized nanofabrics are well suited for the fabrication of textiles with bactericidal surfaces after irradiation by visible light.

*Representative publications*

1. Lang K., Mosinger J., Wagnerová D. M., Photophysical Properties of Porphyrinoid Sensitizers Noncovalently Bound to Host Molecules; Models for Photodynamic Therapy, *Coord. Chem. Rev.* 2004, 248, 321-350.
2. Kubát P., Lang K., Cígler P., Kožíšek M., Matějček P., Janda P., Zelinger Z., Procházka K., Král V., Tetraphenylporphyrin-Cobalt(III) bis(1,2-Dicarbollide) Conjugates: From the Solution Characteristics to Inhibition of HIV Protease, *J. Phys. Chem. B* 2007, 111, 4539-4546.
3. Lang K., Bezdička P., Bourdelande J. L., Hernando J., Jirka I., Kovanda F., Kubát P., Mosinger J., Wagnerová D. M., Layered Double Hydroxides with Intercalated Porphyrins as Photofunctional Materials: Subtle Structural Changes Modify Singlet Oxygen Production, *Chem. Mater* 2007, 19, 3822-3829.
4. Mosinger J., Jirsák O., Kubát P., Lang K., Mosinger B., Jr., Bactericidal Nanofabrics Based on Photosensitized Formation of Singlet Oxygen, *J. Mater. Chem.* 2007, 17, 164-166.
5. Lang K., Kubát P., Mosinger J., Bujdák J., Hof M., Janda P., Sýkora J., Iyi N., Photoactive Oriented Films of Layered Double Hydroxides, *Phys. Chem. Chem. Phys.* 2008, 10, 4429-4434.

## TECHNICAL REPORT

---

### Solvatochromism of thioxanthone (TX) in the light of CAS PT2 computations

Jean-Pierre MALVAL, Bernadette GRAFF, Patrice JACQUES\*

*patrice.jacques@uha.fr*

Department of Photochemistry, CNRS UMR 7525

University of Haute Alsace, ENSCMu

3 rue Alfred Werner

68093 Mulhouse Cedex – France

This paper is dedicated to Professor Dominique BURGET who infected us with one's enthusiasm for the "butterfly like motion".

Dominique died on March 24<sup>th</sup> 2006 during the explosion at the ENSCMu

#### ABSTRACT

The visible absorption energy ( $\tilde{\nu}_a$ ) of thioxanthone (TX) is studied in 31 solvents well representative of all the possible solute/solvents interactions.  $\tilde{\nu}_a$  is not well correlated to the empirical polarity parameter  $E_T(30)$ , which implies that hydrogen bonding of solvents with TX is not significant. This insensitivity is confirmed by the results obtained with the SCM ( $\pi^*$ ,  $\alpha$ ,  $\beta$ ) method and is quite opposite to the behaviour of the fluorescence ( $\tilde{\nu}_f$ ). The  $\tilde{\nu}_a$  values are properly described by the Onsager theory of solvatochromism, which renders possible an estimation of *i)*  $\tilde{\nu}_a$  in the gas phase, *ii)* the excited dipole moment  $\mu_e$ . Comparison of these experimental values with the corresponding theoretical ones obtained from high level CAS PT2 calculations gives support to the occurrence of a "butterfly like motion" for the TX ground state. Moreover, the solvatochromism of the fluorescence matches the statements of CAS PT2 computations of the excited state.

## INTRODUCTION

Thioxanthone (TX) is a model molecule of the so-called "proximity effect" [1]. The vibronic coupling between the two nearly singlet excited  $n\pi^*$  and  $\pi\pi^*$  results in a large dependence of the photophysical characteristics on the medium polarity. For example, the fluorescence quantum yield ( $\phi_f$ ) increases from 0.00062 in THF to 0.23 in ethylene glycol [2, 3] and the triplet quantum yield is also strongly solvent dependent [4]. Indeed, the fluorescence energy ( $\tilde{\nu}_f$ ) undergoes a large red shift when increasing polarity, proof of a significant increase of the dipole moment upon excitation [2]. Such an increase is in line with the charge transfer character of the transition [5] and with recent CAS PT2 calculations [6]. However, inspection of figure 1 shows that  $\tilde{\nu}_a$  seems to be insensitive to *i*) the polarity, *ii*) specific interaction in the hydroxylic solvents. Such a behaviour was recently noticed but not explained [7]. Indeed, a glance at Table 1 in the present paper is very convincing considering that  $\tilde{\nu}_a = 26\,525\text{ cm}^{-1}$  in Cyclohexane, Ethylacetate, 2-Propanol. This prompted us to investigate more deeply the solvatochromism of the U.V. absorption band.

## RESULTS

First of all, it should be reminded here that solvatochromism deals with the shift of the absorption/fluorescence bands, whose *shape* is supposed to be solvent independent. In other words, the absorption/fluorescence wavelength maximum is easily defined and corresponds to the same species whatever the polarity. This is not mostly the case. Therefore, it is important to assess what wavelength will be retained for the correlations versus the polarity functions. Figure 1 shows the TX absorption band in four representative solvents : Cyclohexane (non polar), Ether (low polar), THF (medium polar) and Methanol (polar and hydroxylic). The TX visible absorption band presents a maximum located at  $\sim 378\text{ nm}$  and a shoulder at  $\sim 360\text{ nm}$ . As the polarity increases the shoulder disappears and the bandwidth slightly increases: this band broadening is normal and results from among other solute/solvents dipole/dipole interactions. However, in Methanol the change of the



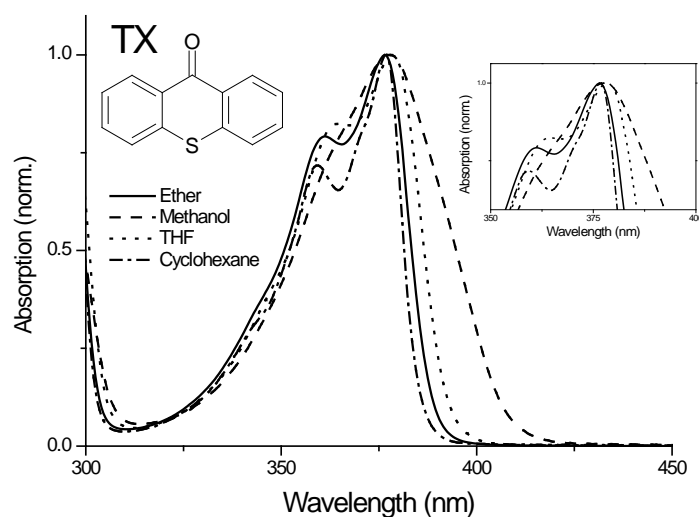


Figure 1 : Visible absorption spectrum of TX in four polarity representative solvents. The spectra are normalized in order to visualize the change of the band shape with polarity. The insert underlines the quasi non-appearance of solvatochromism for these solvents.

band shape is more pronounced on the red side in accordance with the existence of a complex due to hydrogen bonding as reported previously [8]. Anyway, we will retain for each solvent the wave number ( $\text{cm}^{-1}$ ) of the absorption maximum ( $\tilde{\nu}_{\text{max}}$ ) as representative of the TX absorption band. Then, three different models as solvatochromism are applied to the data  $\tilde{\nu}_a = \tilde{\nu}_{\text{max}}$  obtained in 31 solvents well representative of the different solute/solvents interactions : non specific (of physical nature) and specific (hydrogen bonds).

Approaches to solvatochromism are really plethoric [9] and should be critically applied since the appropriate model mostly depends on the chemical structure of the solute. The different models proposed in

the literature can be conveniently reduced to three levels of treatment. Indeed, a thorough description of the solute/solvents interactions is a many-faceted topic for which the level of approach needs a distinction between normal and specific interactions.

Normal solute/solvents interactions only involve multipole and polarisability properties of the solute and solvents molecules. They can be satisfactorily treated in the frame of the continuum model. It characterizes the solvent by its static dielectric constant ( $D$ ), its refractive index ( $n$ ) and the well-known Onsager polarity functions [10, 11] :

$$f(n^2) = \frac{2(n^2 - 1)}{2n^2 + 1} \quad (1)$$

$$f(D) = \frac{2(D - 1)}{2D + 1} \quad (2)$$

This corresponds to the physical approach (non empirical approach). It should be recalled here that the above-mentioned relations (1) (2) totally exclude specific interactions such as hydrogen bonding.

This circumvention of this problem was proved easy by using a totally empirical approach which describes all the possible solute/solvents interactions by use of a single parameter. By far the most famous is  $E_T(30)$ , based on the UV transition energy of a betaine dye [9]. Finally, semi-empirical methods, in fact multilinear approaches have been proposed. The most popular is certainly the Solvatochromic Comparison Method (*SCM*). According to their authors[12], the *SCM* method aims to unravel, quantify, correlate and rationalize all the solvent/solute interactions. This method was intended for use in linear solvation energy relationships (*LSER*) and in its simplest form as :

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta$$

-  $XYZ$  and  $XYZ_0$  are the investigated property in the solvent and gas phase, respectively.

- $\pi^*$  is an index of solvent dipolarity/polarisability which measures the ability of the solvent to stabilize a charge of a dipole by virtue of its dielectric effect.
- $\alpha$  describes the ability of the solvent to give a proton in a solvent to solute hydrogen bond.
- $\beta$  provides a measure of the ability of the solvent to accept a proton in a solute to solvent hydrogen bond.

We will now apply these three different approaches to the absorption maximum wavelength ( $\tilde{\nu}_a$ ) obtained in 31 solvents. Note that the initial set of solvents reported in [2] was considerably extended in order to span the whole polarity scale and different chemical structures of the solvents. By the way, it includes solvents not commonly used such as 1-Chlorobutane, HMPA. Table 1 gathers the  $\tilde{\nu}_a$  values and the polarity data of the solvents. The solvents are classified and numbered conveniently according to increasing value of  $E_T(30)$ .

#### 1. Empirical parameter $E_T(30)$

From just a transitory view of table 1, it is obvious that the  $\tilde{\nu}_a$  dependence on  $E_T(30)$  is not standard.

This is confirmed by figure 2 which reports the  $n=31$  values of  $\tilde{\nu}_a$  versus  $E_T(30)$ . At first sight, no clear trend comes out. The scatter of the data is large. It is only possible to consider that roughly : *i*)  $\tilde{\nu}_a$  is polarity independent for the solvents  $E_T(30) \leq 55$  ; *ii*)  $\tilde{\nu}_a$  is strongly red shifted in the solvents  $E_T(30) > 56$ .

Interestingly, these two features were in fact soon apparent in figure 3 [2], a mere hazard due to the restricted number of solvents. However, we unfortunately overlooked this question at that time. Indeed, it will now be shown that proper treatment of the present 31 absorption values is not trite.

The solvents 12, 26, (ill-behaved) and 28-31 for which severe hydrogen bonds are expected [7] should be excluded, which lead to the following correlation :

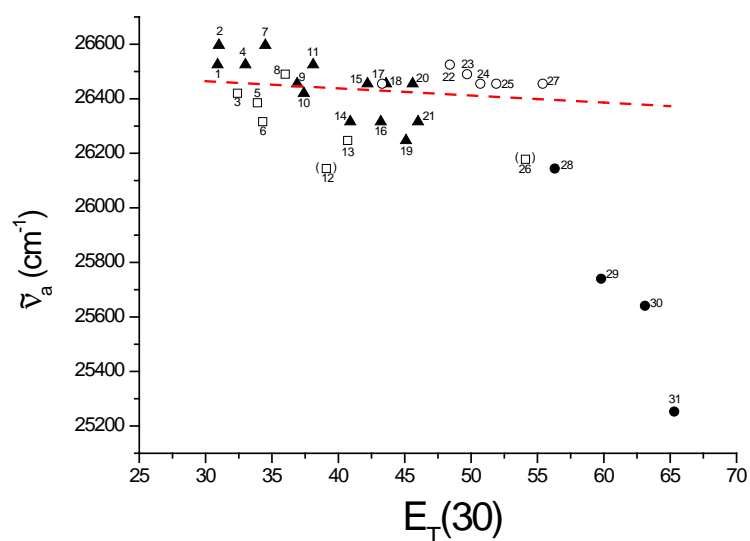


Figure 2:  $\tilde{\nu}_a$  versus  $E_T(30)$  for the entire set of solvents .

▲ : non specific; ○ : alcohols ; ● strong hydrogen bonding ; □, (□) : special (see text). The line corresponds to equation (3):  $\tilde{\nu}_a^{cal} = 26543 - 2.62 E_T(30)$ . Solvents ● and (□) are excluded.

$$\tilde{\nu}_a = (26543 \pm 118) - (2.62 \pm 2.83) E_T(30) \quad (3)$$

$$n = 25 \quad r = 0.1895$$

The slope is low and more importantly has a very large uncertainty which reflects the scatter of the data. It should be noted that according to equation (3) the corresponding absorption wavelengths for the extreme polarities  $E_T(30) = 30$  and  $E_T(30) = 55$  are computed at 377.9 and 378.8 nm respectively, that is only 1 nm red shift.

Indeed, the fact that the alcohols presents very nearly the same  $\tilde{V}_a$  as the non polar solvent, cyclohexane is surprising in view of the large dependence of the other TX photophysical parameters on hydroxylic solvents. Whatever the reasons, it appears that  $\tilde{V}_a$  is not sensible to hydrogen bonding. This should be easily confirmed by the SCM approach.

### 2. The ( $\pi^*$ , $\alpha$ , $\beta$ ) approach (SCM)

It is well known that the parameter  $E_T(30)$  can account for the solute/solvent interactions represented by  $\pi^*$  and  $\alpha$  but not  $\beta$  [9]. It could be therefore suspected that the above mentioned failure of  $E_T(30)$  has to be related to a significant  $\beta$  contribution to the TX solvatochromism. Indeed, the application of the solvatochromic comparative method to the same set of solvents  $n=25$  retained previously gives :

$$\tilde{V}_a = (26\,543 \pm 24) - (343 \pm 46) \pi^* + (14 \pm 39) \alpha + (95 \pm 47) \beta$$

(4)

$$n = 25 \quad r = 0.8659$$

Only the  $\pi^*$  coefficient has a significant value which is negative, indicative of a red shift as the polarity increases.

It appears therefore that *i*) the  $\beta$  contribution is in this case not assessed, *ii*) more importantly, there is no specific contribution at all from the hydroxylic solvents, the  $\alpha$  coefficient vanishes, a result which is somewhat puzzling for a molecule bearing a carbonyl group, but in agreement with the discussion concerning equation (3). In a few words, it can be surmised that the TX solvatochromism of its absorption band is a quite common case governed by non specific interactions. Hence, let us apply the Onsager formalism.

### 3. Physical approach

For an absorption band, the physical approach in its *simplest* form describes the solvatochromic shift as composed by two contributions [11]:

$$\tilde{\nu}_a = \tilde{\nu}_0 - \mathbf{A} f(n^2) - \mathbf{B} f(D, n^2) \quad (5)$$

with :

$$f(D, n^2) = f(D) - f(n^2)$$

$$\mathbf{A} = (\mu_e^2 - \mu_g^2) / 2 a^3 \text{ (Absorption, Fluorescence)}$$

$$\mathbf{B} = \mu_g(\mu_e - \mu_g) / a^3 \text{ (Absorption)}$$

$$\mathbf{B} = \mu_e(\mu_e - \mu_g) / a^3 \text{ (Fluorescence)}$$

$\mu_g, \mu_e$  : dipole moment of the solute in the ground, excited state respectively

$a$  : radius of the solute cavity

In the case where the multilinear regression (5) has high correlation coefficient ( $r^2 \geq 0.9$ ) and the  $\nu_0, A, B$  coefficients low uncertainties, one can get useful experimental estimation of two important characteristics of the solute :  $\mu_e, \tilde{\nu}_a^{gas}$  :

- supposing that  $\mu_g$  is experimentally known (or can be estimated from molecular modelling), it is thus possible to extract from the coefficients **A, B** the dipole moment  $\mu_e$ . This quantity is a key information for photochemists, since it gives precious insights in the electronic distribution of the solute excited state. However, it should be noted that the **A** term reported here is a rough approximation since there are in fact two other contributions : *i*) one related to the variation of the solute polarisability upon excitation, *ii*) the other is due to the transition dipole moment term [10]. Therefore,  $\mu_e$  is exclusively estimated from the **B** coefficient.

- conceptually,  $\tilde{\nu}_0$  corresponds to the transition energy of the solute in the gas phase ( $\tilde{\nu}_a^{gas}$ ). It should be noted however that the relevance of identifying the constant term  $\tilde{\nu}_0$  is the solvatochromic correlations to ( $\tilde{\nu}_a^{gas}$ ) is still under debate.

A proper application of the Onsager relations (1) and (2) to solvatochromism investigations excludes solvents with specific interactions but also solvents which have reputedly abnormal behaviour [11]. Thus, CCl<sub>4</sub>, Toluene, Benzene, Dioxane, CH<sub>2</sub>Cl<sub>2</sub> were subtracted from the precedent set as well as the six alcohols. The following multilinear correlation for the fourteen remaining solvents is :

$$\tilde{\nu}_a = (27\ 663 \pm 94) - (2790 \pm 242) f(n^2) - (345 \pm 32) f(D, n^2)$$

(6)

$$n = 14 \quad r = 0.9788$$

The correlation coefficient is good and the uncertainties of both coefficients low. However, from the results obtained within the ( $\pi^*$ ,  $\alpha$ ,  $\beta$ ) frame, indicating that no specific interactions are at work, it is tempting to include also the six alcohols. Interestingly, the corresponding correlation is admissible :

$$\tilde{\nu}_a = (27\ 600 \pm 136) - (2760 \pm 343) f(n^2) - (325 \pm 48) f(D, n^2)$$

(7)

$$n = 20 \quad r = 0.9176$$

The coefficients are not significantly affected by taking into account the six alcohols which apparently mean that these alcohols effectively behave more or less as normal solvents. Moreover, it is instructive to comment the linear correlations of  $\tilde{\nu}_a$  with only  $f(D, n^2)$  as usually done in most solvatochromism studies found in the literature.

$$\tilde{\nu}_a = (26\ 586 \pm 51) - (352 \pm 112) f(D, n^2)$$

(8)

$$n = 14 \quad r = 0.6705$$

$$\tilde{\nu}_a = (26\ 575 \pm 48) - (274 \pm 98) f(D, n^2)$$

(9)

$$n = 20 \quad r = 0.5512$$

It is clear that this simplified procedure based on  $(D, n^2)$  only gives correlations which are now significantly less valuable than the preceding equations (6) and (7). This in turn implies that  $f(n^2)$  has to be considered and moreover brings an important contribution to the overall shift.

However, it is advantageous to consider more in detail the correlations (8) and (9) obtained with only  $f(D, n^2)$  since a visual representation is possible. Indeed, a glance at figure 3 reveals interesting features. The scatter of the points is large especially in the high polarity range. Four solvents can be discriminated as they induce a larger red shift compared to the others : PC, DMF, HMPA, DMSO. It should be noted that the corresponding  $f(n^2)$  values are high, in agreement with the key contribution of  $f(n^2)$  to the red shift underlined previously.

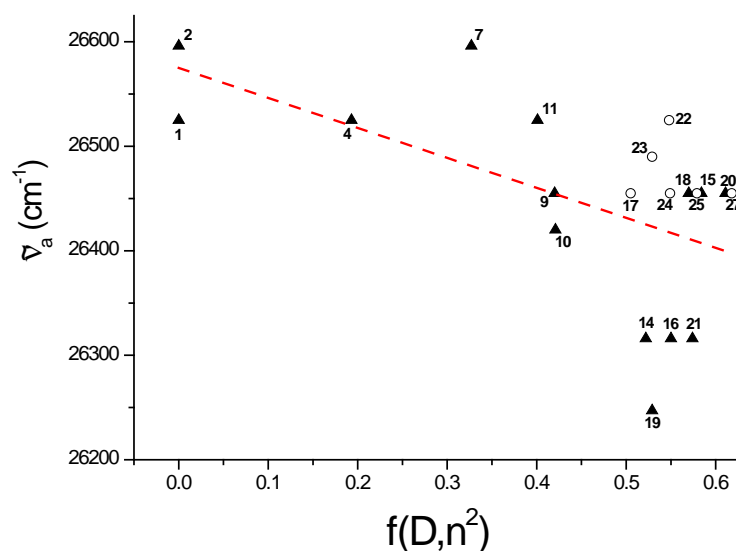


Figure 3 : Solvatochromic plots with  $f(D, n^2)$  only. Note the expanded scale of  $\tilde{\nu}_a$  compared to figure 2.

▲ : non specific ; ○ : alcohols.

$$- \tilde{\nu}_a^{cal} = 26\,575 - 274 f(D, n^2) \text{ equation (9)}$$

## DISCUSSION



### Absorption

Since the  $\tilde{\nu}_a$  solvatochromism is governed by solute/solvents interactions of physical nature, let us take profit of the good relation reported by equation (6), by extracting the two quantities of interest :  $\tilde{\nu}_a^{gas}$  and  $\mu_e$ , with quite evidently, the purpose of comparing them with the theoretical values reported [6]. Therefore, it is necessary to recall here the main features obtained from CAS PT2 calculations : *i*) TX should be viewed as dynamical changing its conformation between non planar (NP) and planar (P) conformation. Moreover, in gas phase the NP conformation is more stable by 0.6 kcal/mol, *ii*) the NP and P conformers have quite different physical properties as summarized in table 2, *iii*) butterfly like motion proved to be persuasive for interpreting as well the "proximity effect" being at the origin of the dramatic dependence of the fluorescence quantum yield on polarity as the UV absorption spectrum.

-  $\tilde{\nu}_a$  in the gas phase

The experimental visible absorption band is  $\tilde{\nu}_a^{gas} \sim \tilde{\nu}_0 = 27\,700$   $\text{cm}^{-1}$  (from eq(6)) is flanked by the two computed  $\pi\pi^*$  transitions of the NP and P conformers obtained in the gas phase, 28 985  $\text{cm}^{-1}$  and 25 840  $\text{cm}^{-1}$  respectively). Keeping in mind that identifying the constant term  $\tilde{\nu}_0$  in the solvatochromic correlations described by eq. 5 to the transition energy of the solute in the gas phase  $\tilde{\nu}_a^{gas}$  is only approximative, it is worth noting that the  $\tilde{\nu}_0$  value obtained from eq.6 is quite different from  $\pi\pi^*(\text{NP})$  and  $\pi\pi^*(\text{P})$ . This fact safely localizes  $\tilde{\nu}_a^{gas}$  between the two computed transition energies of the limit conformers NP and P. Moreover,  $\tilde{\nu}_a^{gas}$  is clearly in better agreement with the CAS PT2 value computed for the more stable NP conformation of TX (28 985  $\text{cm}^{-1}$ ), favoured in the gas phase, than with the computed value for the P conformation (25 840  $\text{cm}^{-1}$ ). We consider these results as germinal hints of *i*) the reliability of the CAS PT2 method, *ii*) the occurrence of the butterfly like motion.

-  $\mu_e$  evaluation

To draw a parallel between the discussions on  $\tilde{\nu}_a^{gas}$  and  $\mu_e$ , it is convenient first to compute the theoretical slopes of the absorption solvatochromism (B coefficient eq. 6) for the NP and P limit conformers. Taking a spherical cavity for TX with Onsager radius  $a = 3.6 \text{ \AA}$ , the computed values of B are  $136 \text{ cm}^{-1}(\text{NP})$ ,  $766 \text{ cm}^{-1}(\text{P})$ , and differ much, by a factor six. Quite interestingly, the experimental slope ( $B = 345 \text{ cm}^{-1}$ , eq. 6) is flanked by the two computed B slopes. Moreover, the experimental  $\mu_e$  derived from solvatochromism ( $B = 345 \text{ cm}^{-1}$ , the experimental  $\mu_g = 2.65 \text{ D}$  [13] is  $4 \text{ D}$ , a value clearly flanked by the two  $\mu_e$  computed values  $5.9 \text{ D}(\text{P})$  and  $2.8 \text{ D}(\text{NP})$  for the limit conformers. We dare see in that result another qualitative confirmation of the butterfly like motion of the TX molecule.

Indeed, the overall solvatochromism of  $\tilde{\nu}_a$  would be a consequence of the convolution between two quite distinct facts. On one hand, in a given solvent, the overall experimental absorption spectrum  $\tilde{\nu}_a$  results from the different  $\tilde{\nu}_a'$  associated with the infinite number of conformations between the P and NP conformers. Unfortunately, to delve into this topic seems unrealistic. Indeed, a quantitative computation of  $\tilde{\nu}_a$  would require an inclusion of the solvent in the CAS PT2 calculations in order to determine the statistical weight of each  $\tilde{\nu}_a'$  *i.e.* a formidable task beyond the scope of the present paper. On the other hand, moreover, changing the solvent would induce a "normal" shift for each conformation but more importantly would change also the statistical contribution of each intermediate conformation.

This situation could moreover explain (at least in part) the absence of an extra redshift of  $\tilde{\nu}_a$  in alcohols due to hydrogen bonding as usually observed for molecules bearing a carbonyl group.

### Fluorescence

In contrast to the preceding discussion concerning  $\tilde{\nu}_a$ , the solvatochromism of fluorescence is entirely normal *i.e.*  $\tilde{\nu}_f$  is strongly affected by hydrogen bonding in alcohols as well known in the literature for a long time. Moreover,  $\tilde{\nu}_f$  is nicely correlated to  $E_T(30)$  [2]. Of great concern with the present study,  $\tilde{\nu}_f$  is also very well correlated with  $f(n^2)$  and  $f(D, n^2)$  in non specific solvents :

$$\tilde{\nu}_f = (28\,300 \pm 550) - (5700 \pm 1400) f(n^2) - (2\,500 \pm 200) f(D, n^2) \quad (10)$$

n = 8            r = 0.9884

The **B** coefficient is here higher by a factor 7 than for the absorption (eq.6). The estimated  $\mu_e$  is now 6.0 D, a value significantly higher (50%) than the value  $\mu_e = 4$  D obtained from absorption solvatochromism. Importantly, from table 2, it is clear that the fluorescence exclusively occurs from a single conformation of the planar P conformer, as expected. In return, the different and too low value  $\mu_e$  (4D) derivated from absorption solvatochromism, flanked by the two  $\mu_e$  values of the limit conformers NP(2.8 D) and P (5.9 D) evidences the presence of many conformers for the TX ground state.

### **CONCLUSION**

Solvatochromism of thioxanthone is in overall agreement with the CAS PT2 investigation very recently reported [6]. The fact that absorption and fluorescence solvatochromism indicates quite different excited dipole moment  $\mu_e$  is a signature of the occurrence of a "butterfly like motion" in its ground state. It is worth underlining that the present paper adds strength to two "old" proposals : *i*) TX is

not planar as was suggested soon in 1972 from a conformational study based at that time on dipole moments considerations [14], ii) phenoxathiin, a molecule strongly related to TX (O atom instead of the C=O group) was also supposed non planar and more importantly it was stated that : "A butterfly flapping motion about the planar conformation cannot be excluded" [15].

N°	Solvent		$\tilde{\nu}_{\text{abs}} (\text{cm}^{-1})$	$E_{\text{T}}(30)$	$\pi^*$
1	Cyclohexane	▲	26525	30.9	0
2	Hexane	▲	26596	31.0	-0.11
3	CCl <sub>4</sub>	□	26420	32.4	0.21
4	Butylether	▲	26525	33.0	0.18
5	Toluene	□	26385	33.9	0.49
6	Benzene	□	26316	34.3	0.55
7	Ether	▲	26596	34.5	0.24
8	Dioxane	□	26490	36.0	0.49
9	1-Chlorobutane	▲	26455	36.9	0.4
10	THF	▲	26420	37.4	0.55
11	Ethylacetate	▲	26525	38.1	0.45
12	CHCl <sub>3</sub>	(□)	26144	39.1	0.58
13	CH <sub>2</sub> Cl <sub>2</sub>	□	26247	40.7	0.82
14	HMPA	▲	26316	40.9	0.87
15	Acetone	▲	26455	42.2	0.62
16	DMF	▲	26316	43.2	0.88
17	<i>t</i> -Butanol	○	26455	43.3	0.41
18	Propionitrile	▲	26455	43.6	0.64
19	DMSO	▲	26247	45.1	1
20	CH <sub>3</sub> CN	▲	26455	45.6	0.66
21	PC	▲	26316	46.0	0.83
22	2-Propanol	○	26525	48.4	0.48
23	1-Butanol	○	26490	49.7	0.47
24	1-Propanol	○	26455	50.7	0.52
25	Ethanol	○	26455	51.9	0.54
26	NMF	(□)	26178	54.1	0.9

27	Methanol	○	26455	55.4	0.6
28	Glycol	●	26144	56.3	0.92
29	TFE	●	25740	59.8	0.73
30	H <sub>2</sub> O	●	25641	63.1	1.09
31	HFIP	●	25253	65.3	0.65

N°	Solvent		$\alpha$	$\beta$	$f(n^2)$	$f(D, n^2)$
1	Cyclohexane	▲	0	0	0.406	0.0
2	Hexane	▲	0	0	0.371	0.0
3	CCl <sub>4</sub>	□	0	0.1	0.428	0.024
4	Butylether	▲	0	0.46	0.388	0.193
5	Toluene	□	0	0.11	0.451	0.028
6	Benzene	□	0	0.1	0.453	0.005
7	Ether	▲	0	0.47	0.354	0.327
8	Dioxane	□	0	0.37	0.404	0.042
9	1-Chlorobutane	▲	0	0	0.390	0.420
10	THF	▲	0	0.55	0.394	0.421
11	Ethylacetate	▲	0	0.45	0.369	0.401
12	CHCl <sub>3</sub>	(□)	0.2	0.1	0.418	0.303
13	CH <sub>2</sub> Cl <sub>2</sub>	□	0.13	0.1	0.405	0.436
14	HMPA	▲	0	1	0.428	0.522
15	Acetone	▲	0.08	0.48	0.359	0.570
16	DMF	▲	0	0.69	0.409	0.550
17	<i>t</i> -Butanol	○	0.42	0.93	0.378	0.505
18	Propionitrile	▲	0	0.37	0.364	0.584
19	DMSO	▲	0	0.76	0.439	0.529
20	CH <sub>3</sub> CN	▲	0.19	0.4	0.347	0.611
21	PC	▲	0	0.4	0.403	0.574
22	2-Propanol	○	0.76	0.84	0.373	0.548
23	1-Butanol	○	0.84	0.84	0.388	0.529
24	1-Propanol	○	0.84	0.9	0.379	0.549
25	Ethanol	○	0.86	0.75	0.361	0.579
26	NMF	(□)	0.62	0.8	0.411	0.581
27	Methanol	○	0.98	0.66	0.337	0.618

28	Glycol	●	0.9	0.52	0.441	0.549
29	TFE	●	1.51	0	0.308	0.637
30	H <sub>2</sub> O	●	1.17	0.47	0.341	0.640
31	HFIP	●	1.96	0	0.296	0.616

Table 1 : Experimental data  $\tilde{\nu}_a$  and solvent polarity parameters.

CAS PT2 Calculations [6]		
Property	Conformer	
	NP	P
$\tilde{\nu}_a$ (cm <sup>-1</sup> )	28 985 (0.070)	25 840 (0.098)
$\pi \rightarrow \pi^*$		
$\mu_g$ (D)	2.22	1.69
$\mu_e$ (D)	2.79	5.92
$\Delta\mu = \mu_e - \mu_g$ (D)	+0.57	+4.23
SOLVATOCHROMISM (This work)		
ABSORPTION		
$\tilde{\nu}_a^{gas} \approx \tilde{\nu}_0$ (cm <sup>-1</sup> )	27 700	
$B$ (cm <sup>-1</sup> ) = $\mu_g(\mu_e - \mu_g)/a^3$		
CAS PT2	136	766
Experimental	345 ( $\mu_e = 4D$ )	
FLUORESCENCE		
$B$ (cm <sup>-1</sup> ) = $\mu_g(\mu_e - \mu_g)/a^3$		
CAS PT2	170	2 683
Experimental	2 500 ( $\mu_e = 6D$ )	

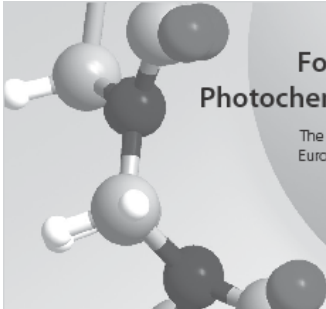
Table 2 : Synoptic theoretical and solvatochromic data. Absorption energies, (oscillator strengths), and dipole moments of the two limit conformers non planar (NP) and planar (P) in gas phase from CAS PT2 calculation. The NP conformer is more stable by 0.6 Kcal/mole [6]. For the  $\mu_e$  evaluation from solvatochromism, the

experimental  $\mu_g$  is considered (2.65 D) and the Onsager radius  $a = 3.6 \text{ \AA}$  (see text). For comparison, the theoretical slopes corresponding to the NP and P conformers are reported.

## BIBLIOGRAPHY

- [1] T. Lai, E.C. Lim, *Chem. Phys. Lett.* 73 (1980) 244-248.
- [2] D. Burget, P. Jacques, *J. Chim. Phys.* 88 (1991) 675-688.
- [3] D. Burget, P. Jacques, *J. Lumin.* 54 (1992) 177-181.
- [4] X. Allonas, C. Ley, C. Bibault, P. Jacques, J.P. Fouassier, *Chem. Phys. Lett.* 322 (2000) 483-490.
- [5] K.H. Giovanelli, J. Dehler, G. Hohlneicher, *Ber. Bunsenges. Phys. Chem.* 75 (1971) 847-863.
- [6] O. Rubio-Pons, L. Serrano-Andres, D. Burget, P. Jacques, *J. Photochem. Photobiol. A: Chem* 179 (2006) 298-304.
- [7] E. Krystkowiak, A. Maciejewski, J. Kubicki, *Chem. Phys. Chem.* 7 (2006) 597 – 606.
- [8] H. Morita, S. Mori, T. Yamaoka, *Bull. Chem. Soc. Jpn* 61 (1988) 191-198.
- [9] C. Reichardt, *Solvents and Solvent effects in organic chemistry*, Wiley-VCH Verlag, Weinheim, 2003.
- [10] P. Suppan, *J. Photochem. Photobiol. A: Chem* 50 (1990) 293-330.
- [11] P. Suppan, N. Ghoneim, *Solvatochromism*, The Royal Society of Chemistry, Cambridge, 1997.
- [12] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R.W. Taft, *J. Org. Chem.* 48 (1983) 2877-2887.
- [13] H. Lumbroso, J. Cure, M. Evers, *Z. Naturforsch* 41A (1986) 1250-1257.
- [14] Z. Aizenshat, E. Klein, H. Feilchenfeld, E.D. Bergmann, *Isr. J. Chem.* 10 (1972) 753-763.
- [15] F.P. Colonna, G. Distefano, V. Galasso, K.J. Irgolic, C.E. King, G.C. Pappalardo, *J. Organomet. Chem.* 146 (1978) 235-248.

## PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



**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.

**PPS provides:**

- High visibility with an impact factor of 2.144\*
- Fast publication times
- RSC Manuscript Central submission system
- No page charges and free colour where it enhances the article

**PPS has a strong themed issue programme, with contributions from key people in the relevant fields. Recent themed issues include:**

- Microscopy beyond Imaging: space-resolved photochemistry and photobiology
- Photosynthesis from molecular perspectives – towards future energy production
- Issue dedicated to Professor NU Turro

**PPS publishes high impact research, recent papers include:**

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

\*2008 Thomas Scientific (ISI) Journal Citation Reports

**Editors-in-chief:**



**Rex Tyrrell**  
Bath, UK  
Photobiology Editor



**Frans De Schryver**  
Leuven, Belgium  
Photochemistry Editor



RSC Publishing



www.rsc.org/pps

Registered Charity Number 307910



## PUBLICATIONS

---

### Abstracts of Theses in Photochemistry

**Andrew McKinley**

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

School of Chemistry, Newcastle University, UK

Supervisor: 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) ligand<sup>1</sup>. 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.

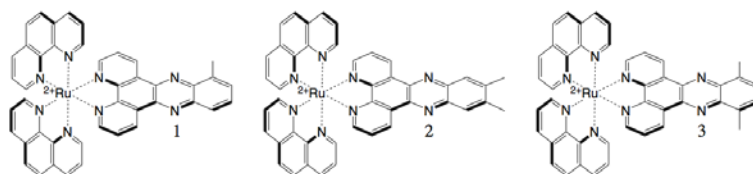


Figure 1:  $\Lambda$ -enantiomers of 10-monomethyl (1), 11,12-dimethyl (2) and 10,13-dimethyl (3) substituted derivatives of  $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ .

---

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

It is generally accepted that the complex binds to DNA by intercalation from the minor groove[2]. 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 [poly(dA-dT)]<sub>2</sub>, where a higher proportion of the longer lifetime is observed at low P/D. However, with [poly(dG-dC)]<sub>2</sub> 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.

Finally, luminescence studies of interactions of [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup> 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 [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup>-flavin complexes binding to polynucleotides shows a possible energy transfer pathway as a function of separation.

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).

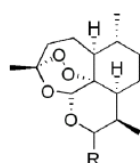
## Angela E. Raabe

### *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, Germany

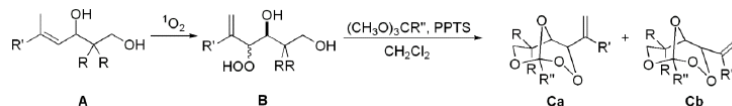
Supervisor: Axel G. Griesbeck

The ene reaction of electronically excited singlet oxygen with allylic alcohols results in  $\beta$ -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.



- R =  $\alpha/\beta$ -OH (Dihydroartemisinin)
- R =  $\beta$ -OMe (Artemether)
- R =  $\beta$ -OEt (Arteether)
- R =  $\alpha$ -OC(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Na (Artesunat)

The synthesis of diols **A** as substrates for the photooxygenation was achieved via enantio-selective 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 photo-oxygenation 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  $\beta$ -hydroperoxy alcohols using orthoesters as carbonyl equivalents. This step was accomplished using *p*-toluene sulfonic acid (as well as BF<sub>3</sub>) catalysts.

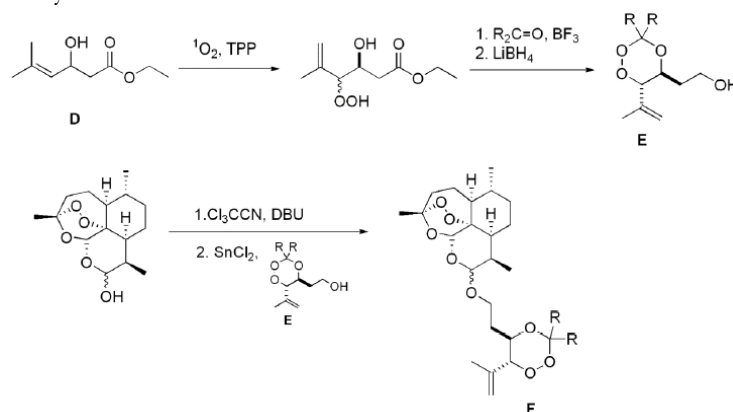


The structure determination was performed by spectroscopic measures together with theoretical calculations (DFT-level) which strongly supported the NMR assignments. The compounds

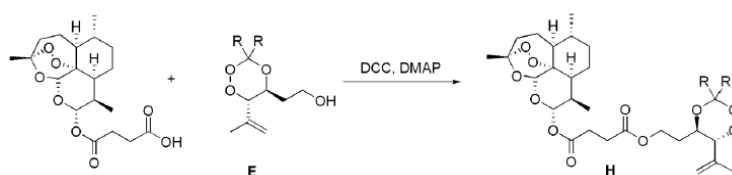
synthesized in this project showed moderate antimalarial activities with about 5% of the artemisinin *in-vitro* activity.

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.

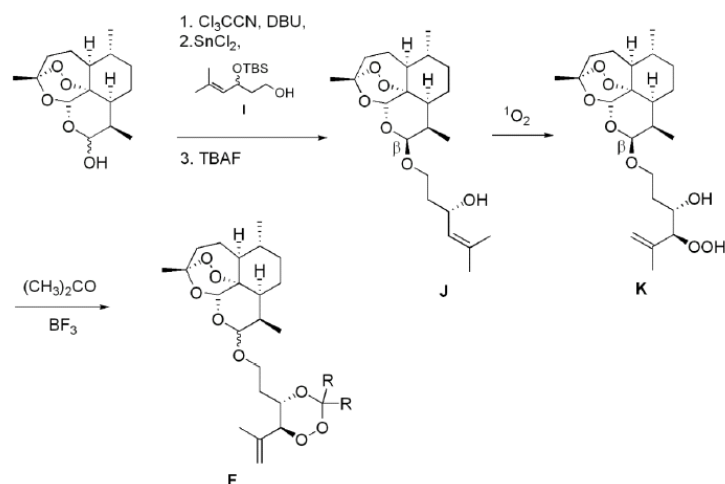
In the first synthetic approach, the aldol adduct **D** was converted in three steps into the 1,2,4-trioxane **E** which was subsequently coupled to dihydroartemisinin.



Esterification of artesunic acid with the same building block **E** resulted in a dual compound **H** where both trioxane pharmacophores 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*

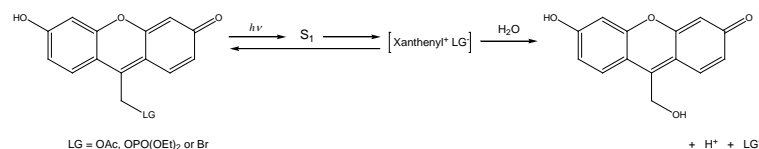
University of Basel, Basel, Switzerland

Supervisor: Jakob Wirz

A new water-soluble photoremovable protecting group for carboxylic acids and phosphates with high molar extinction coefficients ( $\epsilon_{\lambda_{\text{max}}} \sim 25\,000\ \text{M}^{-1}\ \text{cm}^{-1}$ ) 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](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  
Supervisor: Günter Grampp

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: Vincenzo Balzani

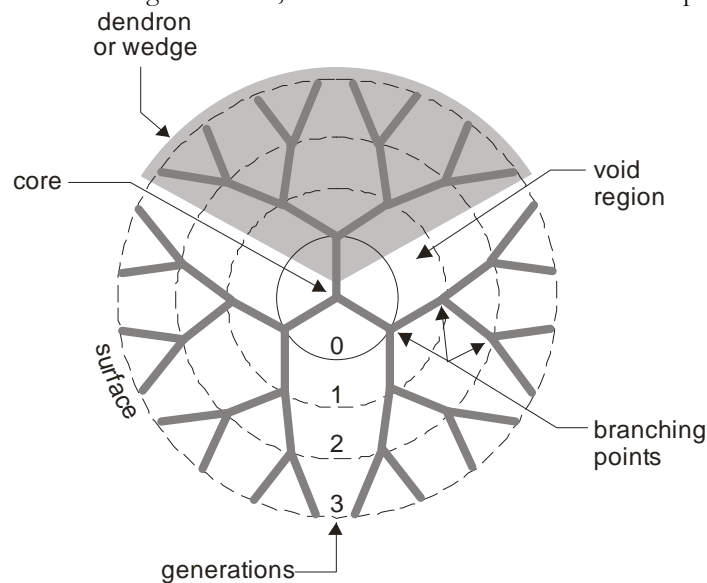
Supramolecular chemistry is “*the chemistry beyond the molecule, bearing on organized entities of higher complexity that result from the association of two or more chemical species*”.<sup>1</sup>

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*.

Dendrimers<sup>2</sup> 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.<sup>3</sup>

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,<sup>4</sup> 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),

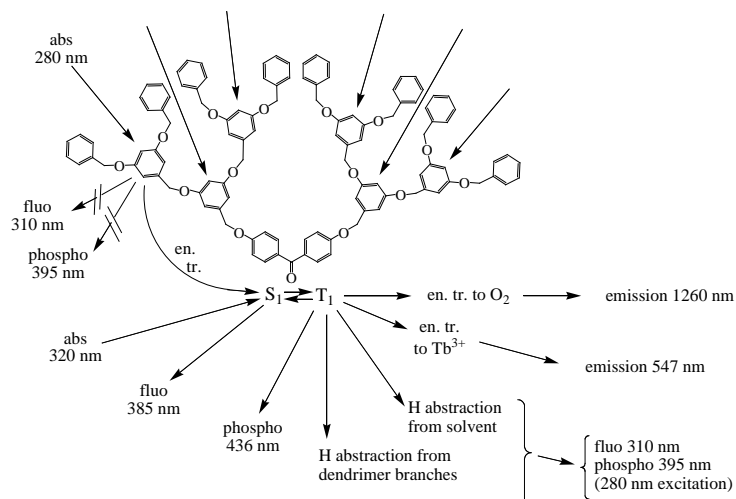
which is particularly interesting for nanotechnology. Furthermore, an increased sensitivity with respect to specific classes of molecules can be established, enabling the detection of very low concentrations of these molecules.

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 data storage.

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 ( $\lambda_x = 320$  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.

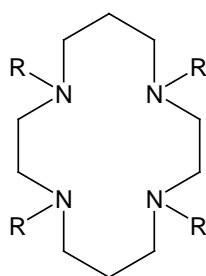
The sensitized  $\text{Tb}^{3+}$  emission observed upon excitation at 320 nm of solutions containing **BBG2** and  $\text{Tb}(\text{CF}_3\text{SO}_3)_3$  shows that the  $T_1$  excited state of the core can transfer energy to the metal ion.<sup>5</sup>

**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  $\text{Tb}^{3+}$  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).<sup>6</sup>

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)



Cyclam core

and, for **CyG2**, naphthyl excimers ( $\lambda_{\text{max}}$  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.<sup>7</sup>

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 ( $\lambda_{\text{max}}$  ca 390 nm), and naphthyl-amine exciplexes ( $\lambda_{\text{max}} = 510$  nm). Titration with  $\text{H}^+$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$  causes strong changes in the emission spectrum and, in the case of  $\text{Cu}^{2+}$ , also in the absorption spectrum. Clear evidence for formation of 1:1 (**BisCyc**.( $\text{H}^+$ ),  $[\text{Zn}(\text{BisCyc})]^{2+}$ ,  $[\text{Cu}(\text{BisCyc})]^{2+}$ ) and 2:1 (**BisCyc**.( $2\text{H}^+$ ),  $[\text{Zn}_2(\text{BisCyc})]^{4+}$ ,  $[\text{Cu}_2(\text{BisCyc})]^{4+}$ ) species has been obtained. The three luminescence bands and, in the case of  $\text{Cu}^{2+}$ , 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.<sup>10</sup>

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.<sup>11</sup>

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  $G_n\mathbf{D}$  family and by energy migration for the  $G_2\mathbf{S}$  dendrimer. In the fourth case, the investigated luminophore (**E**) is non-covalently encapsulated in cavities of a fourth generation poly(propylene amine) dendrimer  $G_4\mathbf{B}$ , containing 1,2-dimethoxybenzene (**B**) units at the periphery. In this case, the study of fluorescence anisotropy of eosin evidenced that eosin rotation inside  $G_4\mathbf{B}$  dendrimer cavities is restricted and that when, as an average, more than one eosin is encapsulated inside a dendrimer, efficient energy migration takes place.<sup>12</sup>

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  $\mu\text{m}$  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.<sup>8</sup>

**References**

1. J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.
2. (a) *Dendrimers and other Dendritic Polymers*, J. M. J. Fréchet, D. A. Tomalia, eds., Wiley, Sussex, **2001**. (b) G. R. Newkome, C. Moorefield, F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Perspectives*, VCH, Weinheim, **2001**.
3. For some recent reviews, see: (a) D. Mery, D. Astruc, *Coord. Chem. Rev.* **2006**, *250*, 1965. (b) D. A. Tomalia, J. M. J. Fréchet, Eds. Special Issue: Dendrimers and Dendritic Polymers. In: *Prog. Polym. Sci.* **2005**, *30* (3-4). (c) V. Balzani, G. Bergamini, P. Ceroni, F. Vögtle, *Coord. Chem. Rev.*, **2007**, *251*, 325.
4. P. Ceroni, G. Bergamini, F. Marchioni, V. Balzani, *Prog. Polym. Sci.* **2005**, *30*, 453, and reference therein.
5. G. Bergamini, P. Ceroni, V. Balzani, F. Vögtle, S.-K. Lee, *ChemPhysChem*, **2004**, *5*, 100.
6. G. Bergamini, P. Ceroni, M. Maestri, V. Balzani, S.-K. Lee, F. Vögtle, *Photochem. Photobiol. Sci.*, **2004**, *3*, 898.
7. G. Bergamini, P. Ceroni, M. Maestri, S.-K. Lee, J. van Heyst, F. Vögtle, *Inorg. Chim. Acta*, **2007**, *360*, 1043.
8. H. Uji-i, S. M. Melnikov, A. Deres, G. Bergamini, F. De Schryver, A. Herrmann, K. Müllen, J. Enderlein, J. Hofkens, *Polymer*, **2006**, *47*, 2511.
10. G. Bergamini, P. Ceroni, V. Balzani, L. Cornelissen, J. Van Heyst, S.-K. Lee, F. Vögtle, *J. Mater. Chem.*, **2005**, *15*, 2959.
11. G. Bergamini, C. Saudan, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, S.-K. Lee, J. Van Heyst, F. Vögtle, *J. Am. Chem. Soc.*, **2004**, *126*, 16466.
12. V. Vicinelli, G. Bergamini, P. Ceroni, V. Balzani, F. Vögtle, O. Lukin, *J. Phys. Chem. B*, **2007**, *111*, 6620.



## Yong Sheng Zhao

### *Preparation and Optoelectronic Properties of Organic Nanomaterials*

Institute of Chemistry, Chinese Academy of Sciences

Supervisor : 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 (Alq<sub>3</sub>) nanowires.** Single crystalline Alq<sub>3</sub> nanowires were prepared with the adsorbent-assisted PVD method, and the Alq<sub>3</sub> 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<sup>-</sup> 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.

[1] Z. Miskolczy, K. Sebők-Nagy, L. Biczók, S. Göktürk, Aggregation and micelle formation of ionic liquids in aqueous solution, *Chem. Phys. Lett.* **2004**, *400*, 296.

[2] R. Vanyúr, L. Biczók, Z. Miskolczy, Micelle formation of 1-alkyl-3-methylimidazolium bromide ionic liquids in aqueous solution, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2007**, *299*, 256.

[3] K. Sebők-Nagy, Z. Miskolczy, L. Biczók, Interaction of 2-Hydroxy Substituted Nile Red Fluorescent Probe with Organic Nitrogen Compounds, *Photochem. Photobiol.* **2005**, *81*, 1212.

[4] Z. Miskolczy, L. Biczók, Fluorescent Properties of Hydrogen-bonded Ellipticine: A Special Effect of Fluorid Anion, *J. Photochem. Photobiol. A, Chemistry* **2006**, *182*, 82.

[5] Z. Miskolczy, L. Biczók, I. Jablonkai, Effect of Hydroxilic Compounds on the Photophysical Properties of Ellipticine and its 6-Methyl Derivative: The Origin of Dual Fluorescence, *Chem. Phys. Lett.* **2006**, *427*, 76.

[6] Z. Miskolczy, L. Biczók, Anion-induced changes in the absorption and fluorescence properties of lumichrome: A new off-the-shelf fluorescent probe, *Chem. Phys. Lett.* **2005**, *411*, 238.

## 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: 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-isoindolinones. 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%.

## Peter Zoon

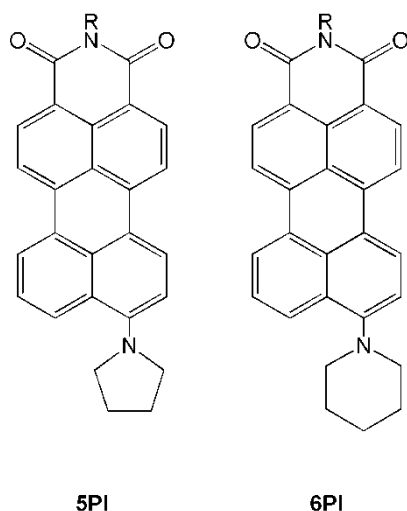
### *Fluorescent Probe Molecules with Individual Detection Capability*

Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Netherlands  
Supervisor: . Fred Brouwer

In this research two new amino substituted push-pull perylene imides were synthesized and the photophysics were studied. The piperidine substituted perylene imide (**6PI**) shows classical push-pull solvatochromic behavior: a moderate shift of the absorption



maximum and a large shift of the emission maximum as function of the solvent polarity. The pyrrolidine substituted perylene imide (**5PI**) shows paradoxical solvatochromic behavior in which it seems that the Stokes shift is negatively dependent on the solvent polarity. To reduce specific solvent solute interactions the solvent polarity of 2-methyltetrahydrofuran was changed by lowering the temperature. These measurements show the same results as a series of solvents of different polarity. The large dipole moment of **5PI**, its high polarizability and a solvent-enhanced donor-acceptor mixing, which reduces the HOMO-LUMO gap, are the explanation for this behavior.



Both probes exhibit excellent single molecule stability with a maximum number of detected photons of 600,000 and survival times in excess of 60 s. These probe molecules are more stable than most commercially available dyes; their stability is only surpassed by quantum dots and unfunctionalized perylene- and terylene imides. Analysis of the single molecule spectra reveal three different types of emitting species: 1) similar to the ensemble spectrum, 2) a highly structured emission, with three distinct emission maxima, 3) a very much blue shifted emission. The very blue shifted species is probably a photoproduct and the highly structured species might be a different

geometrical conformation. Quantum chemical calculations show that population of these states should be rather low.

### References

- [1] P. D. Zoon, A.M. Brauwer, Paradoxical solvent effects on the absorption and emission spectra of amino-substituted perylene monoimides, *ChemPhysChem* **2005**, *6*, 1574-1580.
- [2] P. D. Zoon, A.M. Brauwer, A push-pull aromatic chromophore with a touch of merocyanine, *Photochem. Photobiol. Sci.* **2009**, *8*, 345-353.

## **Celia Paris**

### ***Photophysical and photochemical properties of synthetic nucleosides***

Chemistry Department, Universidad Politecnica de Valencia, Spain  
Supervisor: Susan Encinas

Solar UV-radiation that reaches the Earth-surface is capable of inducing damage to biomolecules, such as DNA, both at the nucleobases and the deoxyribose moiety. Important processes of this type that occur within the cells and may lead to mutagenic events, either direct UVB light absorption by nucleotides, or in an indirect manner, through photosensitized events caused by endogenous and exogenous chromophores (drugs, UV-filters, etc.). The latter molecules can interact with UVA radiation, forming reactive intermediates which would react with DNA. It has been demonstrated that the use of synthetic nucleosides and model systems, are important tools for the study of primary processes involved in DNA photoinduced damage, thus allowing establishing the mechanistic routes for generation of lesions, commonly produced by oxidative or photosensitizing reactions.

The aim of the present doctoral thesis have been to perform photophysical and photochemical studies with model systems (mainly synthetic nucleosides) in order to establish the mechanisms involved in photoinduced DNA damage at the nucleobase and the sugar moiety. The attention has also been focused on the photoinduced repair of tandem lesions such as DCP and (6-4) photoproducts. In particular, as an original concept, it has been considered interesting to

explore the possibility that the photosensitizing and photoprotective activities could be related and therefore present at the same molecule. Elucidation of the mechanisms would allow modulation of the photosensitizing and photoprotective properties, in order to tune the chromophore activity.

In the next paragraphs, the most important experimental results obtained during the course of this doctoral thesis are summarized.

The nature of the photoproducts obtained from photolabile deoxyguanosine derivatives with a NHPT group at the O<sup>6</sup> nucleobase position, depends on the presence of hydrogen donors in the reaction media. The major transient intermediate detected in these dyads is the triplet excited state of 6-[(1-oxide-2-pyridin)-thio](2'-deoxy)guanosine and 6-[(2-pyridin)thio]-(2'-deoxy)guanosine, with an energy appropriate for energy transfer singlet oxygen generation, in DNA. A simpler photochemistry is reported for the 2-hydroxypyridine-2'-deoxyguanosine analogs, with formation of 2'-deoxyguanosine, 2-hydroxypyridine and oxazolone as the main photoproducts formed after UVA steady-state photolysis. Selective and specific generation of the 2'-deoxyguanosine neutral radical [G(-H)<sup>•</sup>], is achieved by homolytic cleavage of N-O covalent bond, without interferences due to reactive oxidative species, such as superoxide radical anion.

On the other hand, photosensitized UVA irradiation of Ketoprofen-Purine dyads generates a 2-deoxyribonolactone derivative, through a mechanism involving intramolecular electron transfer from the nucleobase to the benzophenone-like chromophore present in the dyads. This is followed by a proton transfer process, leading to a biradical intermediate which contains a C1' sugar radical center. Detection is then achieved by the ketyl radical located in the benzophenone chromophore. The principal advantage that these dyads present, is the possibility of studying the reactivity of C1' sugar radicals, by a simple and efficient method.

Regarding the possibility that photosensitizing and photoprotecting properties could be located at the same molecule it has been found that Avobenzone, a widely used UV-filter, is an efficient photosensitizer of DNA nucleosides. The triplet excited state of its diketo form is capable of inducing both thymine dimers (T<>T) formation by energy transfer and guanine oxidation either by an photoinduced electron transfer with generation of G(-H)<sup>•</sup> or

through reaction with singlet oxygen (formed by energy transfer between Avobenzone and molecular oxygen). On the other hand, for the case of a Carprofen derivative (PPMe), it has been demonstrated that this compound induces cyclobutane pyrimidine dimers (DCP) but it also mediates the cycloreversion of (6-4) photoproducts. The mechanism of the former process involves an energy transfer from the higher vibrational energy levels of PPMe triplet excited state, while in the latter case, repair is achieved by an electron transfer from the singlet excited state of PPMe to the oxetanes intermediates, ultimately leading to cycloreversion.

## Izabela Franssen

### *Laser spectroscopy, photophysics and photochemistry of selected electron donor-acceptor systems*

Institute of Physical Chemistry, Polish Academy of Sciences,  
Warsaw

Supervisor: Jerzy Herbich

In this work, we examined the spectroscopic, photophysical and photochemical properties of a series of dialkylaminopyridines which are representative of the electron donor-acceptor (D-A) systems. Investigations were performed in solutions as well as in a supersonic molecular beam. The studied compounds differ in ground state geometry, size of the alkyl substituents (methyl, ethyl, isopropyl) in the donor group and the position of the donor group with respect to the acceptor nitrogen atom (*meta* and *para* isomers), which allowed for comparative investigations of their spectroscopy and photophysics in solutions of different polarity and proton-donating ability. In particular, our studies involved the determination of the electronic structure and geometry of these systems in various electronic states, the examination of the influence of solvation and microsolvation on photo-induced charge transfer (CT) processes and the identification of the properties and structure of molecular clusters (especially hydrogen-bonded complexes) isolated under supersonic molecular beam conditions.

**In solutions**, studies of absorption and magnetic circular dichroism in the UV-Vis range and quantum chemical

calculations allowed for the identification of the nature and lowest excited singlet state energies of the species of interest.

The quantitative analysis of the radiative charge recombination (exemplified by the fluorescence from the excited CT state) in *para* isomers suggests that in those systems emission originates from the TICT state (*i. e.* the structure of the fluorescent CT state consists of mutually twisted  $\pi$ -electron systems  $D^+$  and  $A^-$  to orthogonal conformation). Bimodal kinetics of the process of charge separation in the excited state were identified, with particular attention for the effect of the environment (such as polarity and proton-donating ability) on the rate of this process.

In protic and mixed (hexane + 1-butanol) solvents a strong influence of hydrogen bonds on the spectroscopy and photophysics of the investigated molecules was observed. The mechanism of efficient fluorescence quenching in alcoholic solutions was clarified. It was demonstrated that complexes of a 1:1 stoichiometry and a structure in which an alcohol molecule forms a hydrogen bond with a pyridine nitrogen atom show dual fluorescence, from the primary excited state and the TICT state. An interesting result of this work is the observation of TICT fluorescence in the cation of 4-diisopropylaminopyridine. In the future, this will enable the investigation of the kinetics of the “charge shift” type reaction (contrary to the charge transfer process in neutral forms).

It was shown that 3-diisopropylaminopyridine, in contrast with *para* isomers, upon electronic excitation forms the CT state with a partial charge transfer. This CT state, in contrast with the TICT state, is characterized by an electronic and molecular structure which depends on the properties of the environment.

**Under conditions of isolation in a supersonic molecular beam**, the influence of the excitation energy and geometry of *para*-dialkylaminopyridines on their fluorescence properties was investigated. The emission of the molecules, upon an excitation in the neighborhood of the 0-0 transition, originates from the primary excited state. In the case of a molecule which is characterized by a “twisted” geometry already in the ground state, an excitation with a certain excess energy leads to the appearance of the TICT emission band.

The stoichiometry, structure and luminescence properties of complexes of the investigated compounds with water and a series of alcohols of different acidities were identified. The identification of

the structure of complexes of a 1:1 stoichiometry (hydrogen-bonded to the pyridine nitrogen atom) was possible due to the comparison between experimental results obtained with double-resonance laser spectroscopy and quantum chemical calculations. Fluorescence spectra of these complexes with solvents of relatively low gas-phase acidity (water, methanol and ethanol) show a single band, attributed to the locally excited state. On the other hand, complexes with 1-propanol, 2-propanol and 1-butanol show also the emission from the TICT state.

## Hubert Piwoński

### *Single-molecule fluorescence microscopy of carbocyanine (DiIC<sub>18</sub>) and porphycene dye in thin polymer layers*

Institute of Physical Chemistry, Polish Academy of Sciences

Warsaw

Supervisor: Jerzy Sepiol

The first part of this thesis concerns the problem of oxygen influence on the triplet quenching and photobleaching of a single dye molecule embedded in a polymer matrix. Experiments showed that a well-chosen concentration of oxygen (~2%) in the gaseous environment above the sample efficiently improves the conditions for the single molecule detection. Contrary to common beliefs, an inert, oxygen-free atmosphere is not necessarily the optimal choice for single molecule detection.

The second part is devoted to the search for the evidence of tautomerization in a single molecule of porphycene. The exchange of the two inner hydrogen atoms between the nitrogen atoms in this molecule leads to a chemically equivalent structure, which, however, differs in the position of the transition dipole moments. Experimental approach was based on the analysis of spatial patterns of the fluorescence emitted by single porphycene chromophores excited by using the azimuthally polarized laser beam. Ring shape emission patterns, observed for several single porphycene molecules, could not be explained with the assumption of a fixed transition moment direction. A model that was able to

reproduce exactly the observed fluorescence patterns had to take into account at least two transition moments, with their directions forming a large angle, about  $72 \pm 3^\circ$ . This is just the situation expected for two interconverting *trans* tautomers. The angle between these transition moments was found to be in the excellent agreement with the one obtained from fluorescence anisotropy studies performed for porphycene in rigid polymer.

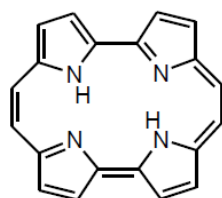
## Natalia Urbańska

### *Synthesis and spectroscopy of multifunctional porphycene derivatives*

Institute of Physical Chemistry, Polish Academy of Sciences  
Warsaw

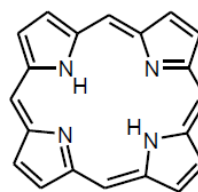
Supervisors: M. Pietraszkiewicz  
J. Waluk

The PhD thesis is dedicated to porphycenes – unique molecules with interesting chemical and physicochemical properties. Porphycene (1) is the first synthesized structural isomer of porphyrin (2).



porphycene

1



porphyrin

2

Porphycene and its derivatives have been objects of physicochemical research for years. A very ambitious and challenging task for every organic chemist is to synthesize new derivatives and to elaborate the high-yield synthesis, which would make it possible to use porphycenes in the physicochemical studies, in medicine or as an alternative substrate in organic syntheses.

This work presents syntheses and properties of differently substituted porphycene derivatives. An easy-to-use and highly productive synthesis method of unsubstituted porphycene (1) was proposed. In addition, an easy-to-use and cost-effective method of the formation of unstable and readily self-oxidising 2,2'-bipyrrole, precursor in porphycene synthesis, has also been proposed.

Most of the synthesised porphycenes were investigated by different methods: electronic absorption and magnetic circular dichroism (MCD) spectra were taken, quantum yields of fluorescence and fluorescence lifetimes were estimated. Spectroscopic measurements allowed classifying porphycene derivatives and helped obtaining deeper understanding of the influence of alkyl substituents, as well as of the position of substitution on the electronic structure of the molecule.

The results of the studies indicate different influence of alkyl substitutes in  $\beta$  and *meso* positions: 2,7,12,17 and 9,10,19,20, respectively. The electronic effects play a dominant role compared to steric effects. Introducing alkyl groups into the *meso* positions of porphycene influences the electronic structure of the molecule, which is manifested by substantial shifts of the absorption bands towards longer waves, whereas, introducing alkyl groups into  $\beta$  positions results in very insignificant changes.

*Meso*-substituted porphycenes are characterised by biexponential fluorescence decays regardless of temperature and solvent. Two different decay times provide evidence of the presence of two different tautomeric forms - *trans* and *cis*. Molecular beam experiments confirm the existence of these forms in 9,10,19,20-tetramethyl- and 9,10,19,20-tetrapropylporphycene. The possibility of synthesis of differently substituted derivatives allows controlling the porphycene cavity dimensions. Such a manipulation makes possible changing of N-N distance, which plays the crucial role in the tautomerization process.



---

## Books

### Review: Photochemistry of Organic Compounds: From Concepts to Practice

*Authors: Peter Klán and Jakob Wirz*

Anyone who has experienced so-called *All Inclusive* holidays will remember the mealtimes – if there were any, rather than having the opportunity to eat 24/7. Usually *All Inclusive* means that food comes in the form of a large buffet where you can pick whatever you like to eat. *Peter Klán's* and *Jakob Wirz's* work “**Photochemistry of Organic Compounds: From Concepts to Practice**” somehow resembles such an *All Inclusive* buffet: It is a pretty vast table filled with every topic in photochemistry one can desire to find.

If you like basic concepts of photophysics you will enjoy chapter two which deals not only with photophysical processes in general, but also introduces the reader to some primary photoreactions such as *energy transfer*, *quenching* and *sensitization*. If you come from a more practical, yet still physical field of photochemistry, you might dig chapter three, which deals for 70 pages with techniques and methods exclusively. You will find every state-of-the-art technique here, from *flash photolysis* to *two-photon absorption spectroscopy*. To round up the “meal” for scientists with higher interest in the physical aspects of photochemistry, chapter four offers the reader some insight into quantum mechanical concepts that might be used in photochemistry.

Return to the picture offered in the first paragraph of this review. More physically and theoretically interested scientists could be considered *herbivorous* (without any judging implied in this term). We shall now turn to *carnivorous* guests at our buffet – those scientists active in the broad field of synthetic photochemistry: Chapter five represents more of a cross section between herbivores and carnivores, say a type of mushroom, consisting mostly of theoretical descriptions of photochemical reaction mechanisms. At the same time it is an entrée to what follows, because in chapter six we find a rich plate of meat; on almost 250 pages Klán and Wirz present an extremely detailed compendium of photochemical reactions – most of them being synthetically relevant – ordered by functional groups:

Alkenes and alkynes, aromatic compounds, oxygen/nitrogen/sulphur compounds and so on. This is surely a great meal to feast on for all synthetic photochemists.

Before we get to the almost 1600 references – the encyclopedia-like menu if you wish to stay in the picture – there is a special chapter seven about retrosynthetic photochemistry as well, consisting of neatly arranged charts which pinpoint exactly which section in chapter six to find the desired reaction.

What, in addition, makes “**Photochemistry of Organic Compounds: From Concepts to Practice**” worthwhile are two special features appearing as insertions in almost every chapter: “*Special Topics*” deal with various specialized aspects of photochemistry, such as *OLEDs*, *electron transfer in biopolymers*, *atmospheric photochemistry* or *artificial photosynthesis*, every occurrence embedded in the chapter being most relative to the special topic’s content. “*Case Studies*”, on the other hand, presents insight into practical aspects throughout most sections – admittedly most of them are to be found in synthetic photochemistry’s chapter, but this prevalence seems nothing but natural. Returning to the “buffet picture” that I tried to carry through this review, imagine these two special features as the spice of the meal presented to you – this is what makes photochemistry tasty.

“**Photochemistry of Organic Compounds: From Concepts to Practice**” has another feature of an *All Inclusive* buffet that might count as a plus for all who are interested – you may pick what you like best. If you like vegetables – forget about the meat and concentrate on chapters two to four; if you are carnivorous to the bone – forget about the greenstuff and enjoy chapters five to seven. Either way will not provide balanced nutrition, but be sure to become replete with whatever you choose to eat.

*Falk Wehmeier*

## 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 Aalders 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-Marzán 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-Marzán, 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](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'énergie 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  $\text{TiO}_2$  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 TiO<sub>2</sub>.
- Photocatalysis for preparative purposes as a tool of Green Chemistry. The plenary lecture of H. Kisch, Erlangen, and the posters of Albin'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.

Esther Oliveros

[oliveros@chimie.ups-tlse.fr](mailto:oliveros@chimie.ups-tlse.fr)

André M. Braun

[Andre.Braun@ciw.uni-karlsruhe.de](mailto:Andre.Braun@ciw.uni-karlsruhe.de)

## CONFERENCE REPORTS

---

### **Spring Session of the French Group of Photochemistry (GFP) May 21<sup>st</sup> – 23<sup>rd</sup>, 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 prize 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 deceptively 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.

**Thomas Gustavsson**

Laboratoire Francis Perrin, URA 2453 CNRS, CEA -Saclay, 91191 Gif-sur-Yvette, France

[thomas.gustavsson@cea.fr](mailto:thomas.gustavsson@cea.fr)

GFP contact : [edmond.amouyal@polytechnique.edu](mailto:edmond.amouyal@polytechnique.edu)



## CONFERENCE REPORTS

---

### **Report on the Autumn Meeting of the French Group of Photochemistry**

Ecole Polytechnique, Palaiseau, France, November 26-28, 2008

The autumn meeting of the French Group of Photochemistry (GFP) was held for the first time at the Ecole Polytechnique of Palaiseau, which offers convenient infrastructure and nice surroundings. First of all, it must be underlined that this meeting was perfectly organized by Edmond Amouyal, with the help of other members of the Laboratoire des Solides Irradiés (LSI, Ecole Polytechnique, Palaiseau). Special thanks are due to Aline Ouzounian, Isabelle Taquin for secretary work, Bernard Jouéo and Serge Boiziau who provided the coffee breaks and buffets with high quality natural products.

The opening speech was given by Olivier Homolle, president of the French Chemical Society and BASF France, who discussed "why the public image of chemistry and chemical products is so poor in France?" There is of course no easy answer to this question, but according to O. Homolle media could be, and should be, used in a better way in order to spread a better view of chemistry in France. After this message started the scientific sessions which covered not only traditional aspects of photochemistry, but also many emerging fields in photophysics and photosciences. The first session was devoted to the application of ultrafast spectroscopic techniques in the studies of protein functional dynamics (Jean-Louis Martin, LOB, Ecole Polytechnique, Palaiseau. Plenary lecture) and electron and energy transfer reactions within a photoreceptor of green algae (Johanna Brazard, ENS Paris). Martin Byrdin (IBITECS, CEA Saclay) presented interesting advances in single-shot spectroscopy.

Then the meeting left modern state-of-the-art technologies and went back in time. Actually, a large number of participants attended the meeting to celebrate the 40<sup>th</sup> anniversary of the GFP. For this occasion, four founding members gave talks describing their scientific careers and what advances they have brought to the field of photochemistry. It must be noted that most of them insisted on making their presentation with transparencies and an overhead

projector. Lionel Salem (Université Paris-Sud, Orsay), who has been retired for about 20 years, evoked his first contact with photochemistry and the keystone equation:  $\overset{h\nu}{\rightarrow} A^* \rightarrow B$ . In contrast, Lars Lindqvist (LPPM, UPS, Orsay) told us about his most recent works on flavine photophysics, while keeping the perspectives for himself. Henri Bouas-Laurent (ISM, Talence) invited us for a cruise amongst the anthracene derivatives that have been widely developed in his team, and finally Sydney Leach (LERMA, OPM, Meudon) took us along for a ride between the stars in his talk about interstellar photochemistry. All these speakers had brought precious black and white photographs taken during former group meetings testifying that, after all these years, all GFP members remained unchanged. This fact also reminded us that the scientific adventure cannot be dissociated from a human dimension. The end of the day was marked by a refined cocktail party. At the friendly request of Edmond Amouyal, Patrice Jacques (DPG, Mulhouse) welcomed the participants by singing *a capella* three arias from famous operas, dedicated to the photochemistry goddess. He offered everybody a genuine moment of humour, artistic beauty and intense emotion.

On Thursday, the first session was essentially devoted to photochromic materials that are attracting more and more attention in the field of optical memories. Instructive talks were delivered on this subject by Jonathan Piard (ENS, Cachan), Arnaud Heynderickx (CINaM, Marseille) and Michel Sliwa (LASIR Lille). Then, Pierre Couleaud (DCPR, Nancy) told us about recent progress in photodynamic cancer therapy requiring highly elaborated photosensitizers. More fundamental studies were not forgotten with the talk of Damien Laage (ENS, Paris) about the reorientation dynamics of water molecules.

The following session dealt with photobiology. The fine presentations of H el ene Pasquier (LCP, UPS, Orsay) and Pascale Chaugenet-Barret (ENS, Paris) were respectively about the cyan and the yellow fluorescent proteins, a topical subject since the discoverers of these proteins have just been awarded the 2008 Nobel Prize of chemistry. Marten Vos (LOB, Ecole Polytechnique, Palaiseau) showed with ultrafast spectroscopy studies that a flavin-based triad system effectively acts as a lightdriven intraprotein nanowire. Then, Isabelle Gosse (ISM, Pessac) explained in a lively talk how she uses fluorescent macrocycles for detecting acetylcholine, a neurotransmitter involved in numerous neurodegenerative diseases.

A flash-presentation followed by a discussion in front of the posters allowed some young researchers - Zuzanna Pawlowska (LASIR, Lille), Matthieu Manceau (LPMM Aubière), Emanuela Berni (ISM, Pessac) and Romain Dagnélie (LFP, CEA, Saclay) - to present their work.

The afternoon of Thursday 27<sup>th</sup> focused on different techniques directly related to photophysical studies or potentially useful for photochemists. It began with a brilliant plenary lecture from Bernard Valeur (CNAM & ENS Cachan) about fluorescence. Interesting anecdotes and etymological precisions were given to shed light on the history of the technique, while present and future applications were enthusiastically evoked. In the following invited presentation, Guylene Costentin (LRS, UPMC, Paris) explained how she uses photoluminescence to identify various chemical sites at the surface of heterogeneous catalysts. Also working on particles, Marc-André Gaveau (LFP, CEA, Saclay) reported on the spectroscopy and dynamics of calcium dimers deposited on rare gas aggregates. Adrien Criqui (DPG, Mulhouse) took examples from photoinitiating systems to remind us that the EPR spin trapping technique is a precious tool to identify radicals generated by a photoreaction. François Hache (LOB, Ecole Polytechnique, Palaiseau) showed that time-resolved circular dichroism was the right technique to study the dynamics of photoexcited naphthol.

The last session of the day was about applied photochemistry. Nathan McClenaghan (ISM, Talence. Invited lecture) described the synthesis and reactivity of photocatenanes, some beautiful supramolecular structures that can be seen like artificial molecular machines. Then, Valérie Marvaud (UPMC, Paris) gave a very clear account of the development of photo-commutable high-spin molecules, whose future applications are expected in the field of nanomagnets. In contrast, the prototype of a diffractive microstructured polymer brought by Christiane Carré (TELECOM Bretagne, Brest) was already in its commercial stage and will hopefully raise a great demand from laser-, airplane- and car-industries. In another area, Alexandra ter Halle (LPMM, Aubière) was interested in the photochemical reactions undergone by pesticides when spread on vegetation and she clearly underlined the role of formulating agents. Thu-Hoa Tran-Thi (LFP, CEA, Saclay) closed the session, showing how surprising encounters, such as that of zeolites and aromatic pollutants, can result in an original advance in

the field of green chemistry. Discussions continued for a long time in front of a buffet, testing the “Beaujolais nouveau”.

The session of Friday 28<sup>th</sup> was devoted to nano- and micro-particles, a field of increasing research activity. Thierry Gacoin (LPCM, Ecole Polytechnique, Palaiseau. Invited lecture) showed the interest of luminescent oxide nanoparticles, the colour of which can be modified by doping. These particles may find applications for biological labelling. Jean-Pierre Galaup (LAC, UPS, Orsay) showed how he traps dye microcrystals with a laser beam and makes them dance, owing to his optical tweezer system. Mireille Blanchard-Desce (LCPM, Rennes. Invited lecture) explained very clearly how molecular engineering can be applied to organized molecular assemblies, in order to design more efficient electro-optical materials. Finally, for her first presentation as a PhD student, Aline Ouzounian (LSI, Ecole Polytechnique, Palaiseau) showed nicely the advantages of new functionalized gold particles with very interesting luminescence properties.

The last session was about electron and energy transfers in connection with their main applications in the field of optoelectronics and solar energy conversion. Agnès Rivaton (LPMM, Aubière) discussed the photostability of active layers in photovoltaic cells and Martine Cantuel (ISM, Talence) described the development of new emissive copper complexes. Jérôme Fortage (LCBPT, UPD, Paris) gave evidence for long distance electron transfers in various donor-spacer-acceptor systems. The last plenary presentation was delivered by Sebastiano Campagna, president of the Italian Group of Photochemistry, who came especially from Messina to speak about light-harvesting antenna systems. The latter were triads as well as supramolecular architectures made of molecular racks to which various chromophores were appended.

In summary, this autumn meeting was very stimulating and successful in promoting emerging subjects. As underlined by Edmond Amouyal in his closing remarks, the role of the meeting was not only to bring together photochemists of France, but also to favour contacts between specialists coming from different photosciences – a necessary development that makes our research field so exciting today. This approach will be better expressed by the new name of the group **GFP2P**, the French Group of Photochemistry, Photophysics and Photosciences, whose next meeting will be hold in Nancy during spring 2009.

**Suzanne Fery-Forgues**

Laboratoire IMRCP (CNRS / UMR 5623)

Université Paul Sabatier, F-31062 Toulouse, France

GFP2P contact : [edmond.amouyal@polytechnique.edu](mailto:edmond.amouyal@polytechnique.edu)

## CONFERENCE REPORTS

---

### **The 40<sup>th</sup> anniversary of the French Group of Photochemistry (GFP)**

Report on a special session during the GFP Autumn Meeting  
Ecole Polytechnique, Palaiseau, France, November 26<sup>th</sup>, 2008

The 40<sup>th</sup> anniversary of the creation of the French Group of Photochemistry (GFP) was celebrated during a special session of the GFP Autumn meeting at Ecole Polytechnique, the most prestigious of the Grandes Ecoles of engineering in France.

*Edmond Amouyal*, president of the French Photochemistry Group, opened the session with a brief historical account. On November 5 1967, Prof. Jean Rigaudy and Pierre Courtot sent a circular letter (projected as a slide), to invite their French colleagues involved in photochemistry at large to join them at a meeting to be held at the Ecole Supérieure de Physique et Chimie Industrielle (ESPCI) in the city of Paris. The response was enthusiastic and two colloquia were organized in April and May 1968 (before the student unrest) to allow the team leaders to expose their on-going topics and outlooks. Thus the French Photochemistry Group was born, Pierre Courtot being the first secretary. Edmond Amouyal showed the list of the founders, now retired. Some of them presented talks, a summary follows:

*Lionel Salem* told the audience how a theoretician of the ground state like him, made his first steps in the excited states that appeared to him as a frightening mystery in the 1968-1970 period. He was encouraged by Paul de Mayo (University of Western Ontario, Canada) then associate professor at Orsay and, later, contacted Hans Schmidt (Zürich, Switzerland) who suggested to start by studying the H abstraction reaction of ketones. He worked with William G. Dauben (University of California, Berkeley, USA) and Nicholas Turro (Columbia University, USA). This cooperation led to establish a correlation diagram where the excited state of the product was correlated with the ground state of the starting material including a surface crossing. This important result was published in the J. Amer.

Chem. Soc. in 1974 and contributed to the fame of Lionel Salem in the community of photochemists. Lionel Salem failed to mention that he is also well known for the concept of "sudden polarization" undergone by alkenes in the S1 state, important for the mechanism of vision... Incidentally, L. Salem noted that "transition state" should be named "transition structure"; he submitted a note on this topic, coauthored with Robert B. Woodward but their paper was turned down by Eyring. Interesting piece of history!

*Henri Bouas-Laurent* (Institut des Sciences Moléculaires, Bordeaux 1 University, Talence) invited the audience to a guided tour of various facets of the contribution of his group to photodimerization within the last 40 years. Among other topics, he focused on the anthracene substrate because of its unique properties: convenient absorption spectrum, dual fluorescence, photochromic and redox properties, solubility of derivatives in common organic solvents, versatility of product structures...The author illustrated the progress of his team by selected examples of intermolecular, intramolecular (non conjugated chromophores), and supramolecular photochemistry. He showed how the anthracene substrate was instrumental, in particular, in demonstrating excimer intermediacy, photochemical synthesis of crown ethers and cryptands, fluorescence probes and modulation of properties by cation complexation...Finally, a few pictures were displayed where some members of the audience could recognize themselves, 30 years ago.

*Lars Lindqvist* (Laboratoire de photochimie et photophysique moléculaire, Paris-Sud University, Orsay) reported the recent investigation of the protolytic reactions in flavoenzymes studied in the ns-ms time scale. Using the 355 nm harmonic of Nd / YAG laser (pulse ca 2 ns) to produce the photoejection, the author examined the deprotonation of the flavine semiquinone (FMNH<sup>•</sup>) in flavodehydrogenase of flavocytochrome b2 at pH 7.5-9.5. FMNH<sup>•</sup> was produced by photoionization of the reduced flavine FMNH2. After its creation, FMNH<sup>•</sup> undergoes a rapid pH modulated deprotonation. This reaction induces a profound spectral change whose kinetics was studied as a function of pH and buffer (tris) concentration. Deprotonation was found to be biphasic with rates of 2-5 x 10<sup>5</sup> s<sup>-1</sup> to 3 x 10<sup>4</sup> s<sup>-1</sup>. Similar results were observed in other oxydases (rat, spinach), confirming and extending the validity of these

data which were rationalized by considering the known 3 D structure of flavocytochrome b2.

*Sydney Leach*, (LERMA, Paris-Meudon Observatory, Meudon), an expert in celestial photochemistry, gave a general talk on topics very distant, indeed, from the other subjects addressed in this meeting. Celestial chemical species such as grains (interstellar dust) or the so-called "metals" such as atoms, ions and molecules are to be found in four main astrophysical sites: a-the solar system with special emphasis on planetary and comet atmospheres, b-stellar atmospheres, c-interstellar clouds and d-regions of space submitted to high density of UV beams. Technical progress due to microscopes and spectrosopes embarked on satellites and spacecrafts (the earth atmosphere is not transparent enough) has allowed us to discover and characterize a number of new chemical species, by absorption, emission and simulation. Since 1968, three to six "molecules" have been discovered each year. Mass spectrometry is particularly used in studying the atmosphere of planets or comet tails. Sydney Leach captured the audience as judged by the numerous questions raised during and after his talk.

At the end of the session a very agreeable cocktail party was organized to honour of the founding members present this day. All the participants raised their glasses for a toast to another 40 years of stunning success for the French Group of Photochemistry.

**Henri Bouas-Laurent**

Institut des Sciences Moléculaires (CNRS / UMR 5255)  
Université Bordeaux 1, 351, Cours de la Libération, F-33405 Talence,  
France

and **Edmond Amouyal**

Laboratoire des Solides Irradiés (CEA-CNRS / UMR 7642)  
Ecole Polytechnique, F-91128 Palaiseau, France

GFP2P contact : [edmond.amouyal@polytechnique.edu](mailto:edmond.amouyal@polytechnique.edu)





**Photo caption:**

From left to right, under the busts of A. M. Ampère and A. L. Lavoisier, the first modern chemist: Lars Lindqvist, Robert Lesclaux, Simone Hautecloque, Sydney Leach, Henri Bouas-Laurent, Lionel Salem and Edmond Amouyal.

## INVITATIONS

---

### **XXIV International Conference on Photochemistry July 19<sup>th</sup> to 24<sup>th</sup>, 2009, Toledo, Spain**

Dear Colleague:

On behalf of the organizing committee, I am pleased to invite you to participate in the upcoming XXIV 24<sup>th</sup> International Conference on Photochemistry, ICP09, which will be held in Toledo (Spain) from the 19<sup>th</sup> to the 24<sup>th</sup> of July 2009. [Website: http://www.icp09-toledo.com/](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](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](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](mailto:conference.icp2009@uclm.es)

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

## INVITATIONS

---

### France Italy Symposium on Photosciences

The 2<sup>nd</sup> joint meeting of the Italian (GIF) and French (GFP2P) groups of photochemistry –both affiliated with the EPA – will be held from December 7 to December 10, 2009 at the Luminy Campus, Marseille, France.

**Chairmen:**

Edmond AMOUYAL (Palaiseau, France)

Sebastiano CAMPAGNA (Messina, Italy)

**Local Organizing Committee:**

Arnault HEYNDERICKX (CINaM, Marseille), Chair

Isabelle COUTURIER-TAMBURELLI (PIIM, Marseille)

Frédéric FAGES (CINaM, Marseille)

Marc GINGRAS (CINaM, Marseille)

Olivier MARGEAT (CINaM, Marseille)

Philippe MARSAL (CINaM, Marseille)

André SAMAT (CINaM, Marseille)

**Invited lectures:**

Dario BASSANI (Bordeaux 1 University, Talence)

Jacques DELAIRE (ENS-Cachan, Cachan)

Claire RICHARD (Clermont-Ferrand II University, Aubière)

Italian invited speakers to be announced

**Keynote lectures:**

Speakers for keynote lectures to be announced

**Website:**

under construction

**Contacts:**

[arnault.heynderickx@univmed.fr](mailto:arnault.heynderickx@univmed.fr)

[campagna@unime.it](mailto:campagna@unime.it)

[edmond.amouyal@polytechnique.edu](mailto:edmond.amouyal@polytechnique.edu)

## INVITATIONS

---

### **Light in Life Sciences Conference 2009**

We are pleased to announce that the inaugural Light in Life Sciences Conference 2009 will be held at the Sebel Albert Park Hotel in Melbourne, Australia from 24 - 27 November 2009.

Recent and ongoing interdisciplinary research into the application of light technologies is accelerating existing and creating new directions in the life sciences. This conference is designed to both inform and build upon these recent advances in pioneering technologies and their applications.

Aimed at Life Science researchers from universities, research institutes and companies, students, and a broader audience of researchers and industry organisations who, in their research or products, have an interest in applying light (fluorescence) based technologies. This conference will bring together a multidisciplinary group of people, working in the fields of chemistry, physics, optoelectronics and biological and medical sciences.

With presenters working at the cutting-edge of life and other sciences, developing instrumentation, probes and methodologies and applying them in genomics, proteomics, bioengineering, cell biology, medical diagnostics and agricultural biotechnology, the Light in Life Sciences Conference 2009 will provide a dynamic forum focussing on world class, timely, innovative research from Australia and around the world.

The program is designed to enable interactions between those involved in fundamental and applied aspects of research through cross-disciplinary interactions.

The Light in Life Sciences (LILS) Conference 2009 is sponsored by the Australian Research Council (ARC), National Health and Medical Research Council (NHMRC), Becker & Hickl GbmH and Macquarie University. The conference coincides with the fifth and final gathering of the 'Fluorescent Applications in Biotechnology and Life

Sciences' (FABLS) Network and encompasses the 3rd Advanced Optical Imaging Workshop.

The organising committee has planned an outstanding program of International and Australian speakers, with an exciting list already confirmed. This Conference is the start of a new phase to carry forward the momentum of the FABLS Network.

Your participation will contribute to the ongoing growth of the vibrant fluorescence community. So register early and save with the Early Bird registration fee.

For details, please check the web site: <http://www.physics.mq.edu.au/research/fluoronet/LIIS09/>

## INVITATIONS

### Molecular Science for Solar Fuel

**International Conference  
Molecular Science  
for **SOLAR FUEL****

**1–5 November 2009**  
Sigtuna, Sweden

**Important dates:**  
Registration: **June 18**  
Abstract submission: **September 4**

Dear colleagues ,

It is a pleasure to invite you to the International Conference "**Molecular Science for Solar Fuel**". This conference will bring together scientists working to develop biological and chemical approaches that utilize solar energy for fuel production. The conference topics include:

natural and synthetic systems for solar fuel	mechanistic aspects of electron and proton transfer
catalysts for H <sub>2</sub> production	photobiological solar fuel production
catalysts for H <sub>2</sub> O oxidation	
hydrogenases and photosystems	

Organizing Committee	Invited Speakers																		
<ul style="list-style-type: none"> <li>• Stenbjörn Styring, Chairman</li> <li>• Leif Hammarström</li> <li>• Peter Lindblad</li> <li>• Ann Magnuson</li> <li>• Fikret Mamedov</li> <li>• Sascha Ott</li> <li>• Villy Sundström</li> </ul>	<table border="0"> <tr> <td>Fraser Armstrong</td> <td>Wolfgang Lubitz</td> </tr> <tr> <td>Eva-Mari Aro</td> <td>Johannes Messinger</td> </tr> <tr> <td>Ally Aukauloo</td> <td>Daniel Nocera</td> </tr> <tr> <td>Gary Brudvig</td> <td>Gilles Peltier</td> </tr> <tr> <td>Daniel Dubois</td> <td>Matthias Rögnér</td> </tr> <tr> <td>Bärbel Friedrich</td> <td>Per Siegbahn</td> </tr> <tr> <td>Etsuko Fujita</td> <td>Licheng Sun</td> </tr> <tr> <td>John Golbeck</td> <td>Michael Wasielewski</td> </tr> <tr> <td>Antoni Llobet</td> <td>Junko Yano</td> </tr> </table>	Fraser Armstrong	Wolfgang Lubitz	Eva-Mari Aro	Johannes Messinger	Ally Aukauloo	Daniel Nocera	Gary Brudvig	Gilles Peltier	Daniel Dubois	Matthias Rögnér	Bärbel Friedrich	Per Siegbahn	Etsuko Fujita	Licheng Sun	John Golbeck	Michael Wasielewski	Antoni Llobet	Junko Yano
Fraser Armstrong	Wolfgang Lubitz																		
Eva-Mari Aro	Johannes Messinger																		
Ally Aukauloo	Daniel Nocera																		
Gary Brudvig	Gilles Peltier																		
Daniel Dubois	Matthias Rögnér																		
Bärbel Friedrich	Per Siegbahn																		
Etsuko Fujita	Licheng Sun																		
John Golbeck	Michael Wasielewski																		
Antoni Llobet	Junko Yano																		

For more information please visit: [www.fotomol.uu.se/solarfuel2009.html](http://www.fotomol.uu.se/solarfuel2009.html)  
or send us email: [solarfuel@fotomol.uu.se](mailto:solarfuel@fotomol.uu.se)

For more information please visit:

[www.fotomol.uu.se/solarfuel2009.html](http://www.fotomol.uu.se/solarfuel2009.html)

or send us email: [solarfuel@fotomol.uu.se](mailto:solarfuel@fotomol.uu.se)



## INVITATIONS

---

### **Light in Life Sciences 2009**

We are pleased to announce that the inaugural Light in Life Sciences Conference 2009 will be held at the Sebel Albert Park Hotel in Melbourne, Australia from 24 - 27 November 2009.

Recent and ongoing interdisciplinary research into the application of light technologies is accelerating existing and creating new directions in the life sciences. This conference is designed to both inform and build upon these recent advances in pioneering technologies and their applications.

Aimed at Life Science researchers from universities, research institutes and companies, students, and a broader audience of researchers and industry organisations who, in their research or products, have an interest in applying light (fluorescence) based technologies. This conference will bring together a multidisciplinary group of people, working in the fields of chemistry, physics, optoelectronics and biological and medical sciences.

With presenters working at the cutting-edge of life and other sciences, developing instrumentation, probes and methodologies and applying them in genomics, proteomics, bioengineering, cell biology, medical diagnostics and agricultural biotechnology, the Light in Life Sciences Conference 2009 will provide a dynamic forum focussing on world class, timely, innovative research from Australia and around the world.

The program is designed to enable interactions between those involved in fundamental and applied aspects of research through cross-disciplinary interactions.

The Light in Life Sciences (LILS) Conference 2009 is sponsored by the Australian Research Council (ARC), National Health and Medical Research Council (NHMRC), Becker & Hickl GbmH and Macquarie University. The conference coincides with the fifth and final gathering of the 'Fluorescent Applications in Biotechnology and Life

Sciences' (FABLS) Network and encompasses the 3rd Advanced Optical Imaging Workshop.

The organising committee has planned an outstanding program of International and Australian speakers, with an exciting list already confirmed. This Conference is the start of a new phase to carry forward the momentum of the FABLS Network.

Your participation will contribute to the ongoing growth of the vibrant fluorescence community. So register early and save with the Early Bird registration fee.

For details, please check the web site: <http://www.physics.mq.edu.au/research/fluoronet/LIIS09/>

## INVITATIONS

---

### Central European Conference on Photochemistry CECP 2010



organized by **EPA** Austria

Sunday, February 7 to Thursday, February 11, 2010, Bad Hofgastein



Venue:  
Bad Hofgastein, Congress Center

For more information please see:

[www.ptc.tugraz.at/gastein](http://www.ptc.tugraz.at/gastein)

Local coordinator: Dr. S. Landgraf, Graz University of Technology

## INVITATIONS

---

### **6th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA6)**

We are pleased to invite you to attend the **6th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA6)**, to be held at **Masarykova kolej** in Prague, Czech Republic from June 13th to 16th, 2010.

#### **ORGANIZERS**

SPEA 6 is organized jointly by

- Institute of Chemical Technology, Prague (ICT Prague)
- Jaroslav Heyrovský Institute of Physical Chemistry, Academy of Science (JH IPC)

#### **MAIN TOPICS**

The conference will deal with the following topics:

1. **Water treatment and disinfection**
2. **Air treatment**
3. **Environmental photochemistry**
4. **Photoprocesses utilizing solar light**
5. **Development of new materials for photochemistry and photocatalysis (visible light active photocatalysts, composite materials)**
6. **Models for photochemistry and photocatalysis (mechanistic studies, engineering modelling)**
7. **Commercial applications, standardization**

For more information see <http://www.spea6.com/>

## MEMBERSHIP APPLICATION FORM

---



### EUROPEAN PHOTOCHEMISTRY ASSOCIATION 2009 MEMBERSHIP RENEWAL/APPLICATION FORM

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

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

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

Family name: \_\_\_\_\_ First name: \_\_\_\_\_ Middle initial(s): \_\_\_\_\_

Date of birth (dd/mm/yyyy): \_\_\_\_\_

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

Address: (Please use your institutional address)

Tel: \_\_\_\_\_

Fax: \_\_\_\_\_

Email: \_\_\_\_\_

#### Membership fees for 2009 in EUR

(please check one box)

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

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

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

#### Alternative methods of Payment

(please fill in either 1. or 2.)

<p>1. <b>Credit card.</b> Please fill in the details below (all details compulsory). I, the undersigned, authorise the European Photochemistry Association to debit my credit card:</p> <p><input type="checkbox"/> MasterCard                      <input type="checkbox"/> Visa</p> <p>Card number _____                      Expiry date: _____                      For the sum of _____ EUR</p> <p>Amount of EUR in words: _____</p> <p>Name of card holder: _____                      Signature of card holder: _____</p> <p>Security code: ___ (this code corresponds to the last three digits to the right on the back of your credit card)</p>				
<p>2. <b>Bank order</b> to UBS AG, Roemerhofplatz 5, P.O. Box 38, CH-8030 Zürich, BIC (Swift): UBSWCHZH80A Account holder: European Photochemistry Association, c/o Dr. Silvio Canonica, 8600 Dübendorf IBAN: CH27 0025 1251 8404 5260 C</p> <p>I herewith certify that I effected a bank transfer on _____ (fill in date) for the sum of _____ EUR to cover the EPA membership fee for the year(s) 2009 - _____ . Signature of the member: _____</p> <p><b>Please ensure that you are clearly identified on the bank order.</b></p>				