

European Photochemistry Association

NEWSLETTER

December 2010

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Newsletter Editor: Prof. Bo Albinsson

Department of Chemistry and Biological Engineering, Chalmers University of Technology, 412 96 Göteborg, SWEDEN

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EPA EXECUTIVE COMMITTEE



President

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 Email: eric.vauthey@unige.ch



Industry-Liaison

Dr. John Gilchrist Gilden Photonics Ltd. Unit 13 Telford Court, 9 South Avenue Clydebank Business Park Glasgow, G81 2NR, UK Tel: +44(0)141.952.9475 Email: john.gilchrist@gildenphotonics.com



Treasurer

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



Public Relations

Prof. Dr. Olga Fedorova A.N.Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences 28 Vavilova St., Moscow RUSSIA 119991 Tel: +7 499 135 8098 Email: fedorova@ineos.ac.ru



Past President

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



Responsible for PPS matters:

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



Newsletter Editor:

Prof. Bo Albinsson Department of Chemistry and Biological Engineering Chalmers University of Technology 412 96 Göteborg, Sweden Tel +46(0)31 772 3044 Email: balb@chalmers.se



Associate Editor:

Prof. Julia Pérez-Prieto Molecular Science Institute (ICMOL) Valencia University C/ Catedrático José Beltrán, 2 46980-Paterna, Valencia, Spain Tel: +34-96-3543050 Email: julia.perez@uv.es



Website manager:

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

EDITORIAL

President's Letter

We are at the turning point of two important years for photochemistry. This year, we have celebrated the 50th anniversary of the laser. Although photochemistry can be done without a laser, it is quite evident that our field would have been much less advanced without this remarkable source of light. Without lasers, any photoinduced process faster than a few nanoseconds would still be beyond reach and would just be considered as quasi-instantaneous. Similarly, single molecule spectroscopy and microscopy would still be science-fiction. If lasers brought a lot to molecular photosciences, the opposite is also true. The development of the laser, especially of lasing materials, laser dyes being a nice example, has also benefited a lot from the know-how of photochemists. Moreover, our thirst to fully understand all the details of photoinduced processes taking place in ever more complicated systems has also contributed to the development of lasers with ever better specifications. And, to my point of view at least, photochemistry with lasers is much more fun.

As you probably all know, 2011 will be the International Year of Chemistry. This will be a wonderful opportunity to present our science to a large public, to share our enthusiasm and curiosity, and to ignite sparkles of fascination in the eyes of young people. Maybe lasers will help.

Meanwhile, I hope you will enjoy this issue of the EPA Newsletters. This is the first issue elaborated by the new Editors, Bo Albinsson and Julia Perez-Prieto. As you know, the quality of our Newsletter does not only depend on the editors but also on your contributions. So please keep sending us technical notes, abstracts of theses, conference reports and anything you think should be shared with our community.

Eric Vauthey EPA President

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 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 association.

ARTICLE 7

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

ARTICLE 8

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

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

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

(d) At the request of 20% of all EPA members, an extraordinary meeting of the General Council must be organised, and at least three month's notice given, by the Executive Committee. Due provision must be made for those who can not attend the extraordinary

meeting of the General Council personally to express their opinion in writing and, if necessary, by postal or electronic vote.

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

ARTICLE 9

(a) The Executive Committee administers EPA.

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

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

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

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

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

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

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

signed by the nominee, to the Executive Committee any time up to one month prior to the General Council.

TITLE IV: Finances

ARTICLE 10

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

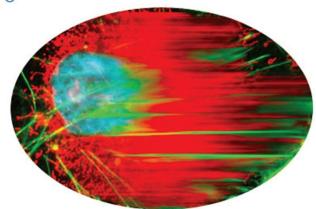
ARTICLE 11

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

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

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



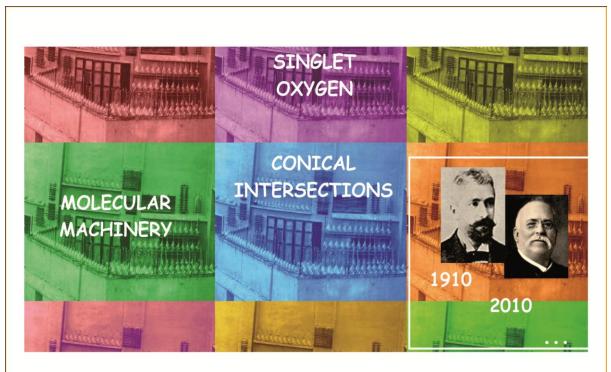


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PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



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PUBLICATIONS

Abstracts of Theses in Photochemistry

Francisco Manjón

Solar technology for water disinfection in rural areas by photosensitized singlet molecular oxygen $({}^{1}O_{2})$ production

Department of Organic Chemistry, Universidad Complutense de Madrid, Spain

PhD Thesis: 2010 Supervisors: Prof. Guillermo Orellana and Prof. David García

Water is a primary need for the human being. Availability of drinking water is a critical problem for an important part of the world population mainly located in less-favored countries where over 1 billion people suffer diseases related to waterborne microorganisms. Classical water disinfection techniques such as chlorination, and less common alternatives based on other oxidizing reagents (ozone, chlorine dioxide, etc.) or physical treatments (membrane filtration or UV-C illumination), are typically used in urban or industrial areas. However, they are difficult to apply in isolated regions or emergency situations, especially those in poorer countries, due to the lack of infrastructures. The so-called solar disinfection (SODIS) method is a cheap alternative to obtain pathogen-free water in those areas placed in the solar radiation belt. Such method uses the combined effect of the UV-A component of sunlight plus the infrared-powered temperature increase to inactivate waterborne bacteria. However, it requires plastic bottles (1–2.5 L) limiting the total amount of water treated per day, is not equally effective with all types of bacteria or turbid waters and requires suitable weather conditions.

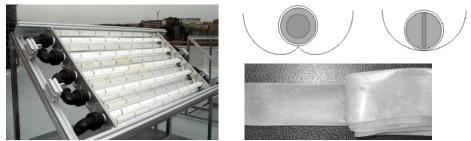


Figure 1. CPC solar reactor for water disinfection by photosensitized singlet molecular oxygen $({}^{1}O_{2})$ production. On the right, a cross-section of the coaxial- and fin-type configurations and a detail of the photosensitizing silicone stripes are shown.

Highly efficient sensitizing materials containing hydrophobic Ru(II) complexes immobilized on porous silicones have been produced, photophysically and photochemically characterized, and successfully tested for inactivation of up to 10^{-4} CFU mL⁻¹ of waterborne *Escherichia coli* (gram-negative) or *Enterococcus faecalis* (gram-positive) bacteria. Two solar reactors based on compound parabolic collectors (CPC) were built (Figure 1) and optimized for water disinfection by photosensitized singlet oxygen ($^{1}O_{2}$) production in heterogeneous phase (Figure 2). The main factors determining the performance of the solar reactors are the type of photosensitizing material, the sensitizer loading, the CPC collector geometry (fin- *vs.* coaxialtype), the fluid rheology and the balance between concurrent photothermal-photolytic and $^{1}O_{2}$ effects on the microorganisms inactivation. In this way, at the 40°N latitude of Spain, water can be disinfected in a sunny day (0.6–0.8 MJ m⁻² L⁻¹ accumulated solar radiation dose in the 360–700 nm range, typically 5–6 h of sunlight) with such CPC-based reactors containing 0.6 m² of photosensitizing material saturated with tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) (RD3, *ca.* 2.0 g m⁻²). The optimum rheological conditions require laminar-totransitional water flow in both prototypes. The fin-type system showed better inactivation efficiency than the coaxial reactor due to a more important contribution of the direct sunlight effect that adds on top of the photodynamic disinfection. The durability of the sensitizing materials was tested and the operational lifetime of the photocatalyst is at least three months without any reduction in the bacteria inactivation efficiency. Moreover, recharging of the used photosensitizing materials with the photoactive dye leads to higher water disinfection efficiency [5]. Solar water disinfection with ¹O₂-generating films is demonstrated to be an effective technique for point-of-use water disinfection in isolated regions of less-favored countries with high yearly average sunshine.

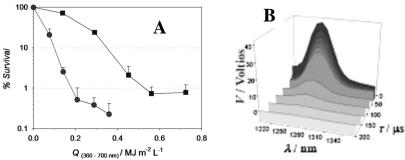


Figure 2. (A) Survival of waterborne *E. faecalis* (10^4 CFU mL⁻¹) in the coaxial-type (\blacksquare) and the fin-type (\bullet) solar reactors containing the photosensitizing stripes. (B) Singlet molecular oxygen ($^{1}O_{2}$) produced by RD3 immobilized in porous silicone (2 g m⁻²) when immersed in water ($\tau_{\Delta} = 32 \mu$ s).

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Benjamin Probst

Photochemical Hydrogen Production

Institute of Inorganic Chemistry, University of Zurich

PhD thesis: 2010 Research Advisor: Prof. Robert Alberto

The splitting of H_2O by sunlight is an attractive scenario to obtain chemical fuels in the postfossil society. Thus research focusing on alternatives to the well established, but indirect route, i.e. using photovoltaics and electrolysis, deserves attention. An especially appealing way is the mimicking of natural photosynthesis, i.e. photochemical water splitting. Much effort has been put into doing so, both in the area of heterogeneous and homogeneous photocatalysis. Common to all approaches in the field of homogenous photocatalytic water splitting is the separation into an oxidative and a reductive halfreaction, and thus the use of sacrificial electron acceptors resp. donors. The idea in doing so is that the two half-reactions can be studied and optimised independently, and once successful candidates were identified, attempts to combine the systems can be undertaken. In this work we focused on the reductive halfreaction to H_2 .

This thesis presents the first successful application of rhenium(I) - tricarbonyl diimine – type complexes ($[ReX(CO)_3 diimine]^+$) as photosensitiser (PS) and cobalt tetraene based water reduction catalyst's (WRC) for the photo induced up-conversion of triethanolamine (TEOA) and protons to oxidised TEOA and H₂ (see Figure 1).

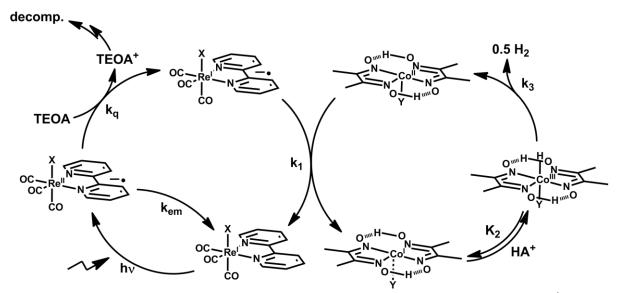


Figure 1. General representation of the photocatalytic cycle using $[ReX(CO)_3bipy]^+$ – type PS's and $[CoY(dmgH)_2]$ – type WRC's to convert TEOA and H⁺ into H₂.

The study focused on various aspects of the new reaction, including the solvent (water, DMF and MeCN), the character of the initial reaction of the excited state, quench rates and yields, spectrochemical properties of the PS, forward electron transfer rates to the cobalt based WRC, kinetics in the WRC cycle, stability of the complexes, influence of pH and quantum yields of H_2 production.

It was shown for systems in DMF^{1,2} by continuous irradiation experiments that $[ReX(CO)_3 diimine]^+$ - type PS's (X = Br⁻, NCS⁻, OH₂ or pyridine; diimine = 2,2'-bipyridine (bipy) or 1,10-phenanthroline) are clearly superior to the commonly used $[Ru(bipy)_3]^{2+}$ PS in terms of catalytic stability. Furthermore, we showed by time resolved IR spectroscopy that the initial photoreaction proceeds by reductive quenching of *[ReX(CO)₃diimine]⁺ by TEOA $(k_q = 5 \times 10^7 \text{ M}^{-1} \text{s}^{-1}; \Phi_{cage} = 0.5)$, followed by fast electron transfer to WRC $(k_1 = 1 - 1)^{-1}$ $2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for WRC = [Co^{II}(dmgH)₂]). In the absence of WRC the transfer of a second reduction equivalent from the decomposition of oxidised TEOA on the rhenium PS was observed ($k_{2,e^-} = 3.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$; 70 %). As for the WRC cycle, fast protonation of Co¹ occurs, as shown by a distinct pH dependence of hydrogen production. The bottleneck of the system appears to be the reaction of Co^{III}-H to H₂, which we could show to occur predominantly in a homolytic fashion for [Co(dmgH)₂] in DMF. Addition of excess free dmgH₂ was required to ensure complete formation of [Co(dmgH)₂] (thermodynamic stability), but also to increase the turnover number in cobalt (TON_{Co}, H_2/Co), possibly due to a self-repair mechanism for deactivated WRC (catalytic stability). The maximum TON_{Re} (H/Re) was 7500, setting a new benchmark, whereas the maximum TON_{Co} was only 1000. This, along with other observations, clearly showed that the performance limiting factor of the system was the cobalt based WRC.

Although these experiments gave a nice proof of principle, drawbacks were, besides the use of sacrificial electron donors, the decomposition of the cobalt based WRC, low overlap of PS absorption to the solar spectrum and the use of organic solvent instead of H_2O . Whereas the issue of using sacrificial electron donors instead of oxidising the substrate of choice, i.e. H_2O , is not yet solved, the progress that has been made recently in the field of photochemical water oxidation^{3,4} should allow to link such a system to a reductive counterpart in theory. Problems to overcome are the solvent (oxidative half-reactions are performed in H_2O , reductive half-reactions in organic solvents), and the set of initial reactions of the excited state, i.e. whether the WOC (water oxidation catalyst) or the WRC interacts with the excited PS.

To address the former issue we designed a series of water soluble, rhenium based PS bearing neutral axial ligands. Initial experiments showed for the fist time that H_2 production from H_2O using the rhenium – cobalt system is principally possible. Kinetic analysis revealed that the initial set of reactions is the same as in DMF solvent, i.e. the reaction proceeds by reductive quenching of the excited PS. No oxidative quenching by the cobalt based WRC was found. Distinct correlations of turnover numbers to the ligand framework of the WRC were observed, allowing the rational design of new catalysts. A systematic screening of $[ReX(CO)_3 diimine]^+$ complexes allowed to understand absorption properties and to optimise the overlap wit the solar spectrum.

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Rajinder Singh

Investigations on photochemical and thermal transformations of some conjugated carbonyl compounds

Department of Pharmaceutical Sciences, Guru Nanak Dev University, Amritsar, India

PhD thesis: 2010 Research Advisor: Prof. Mohan Paul S. Ishar

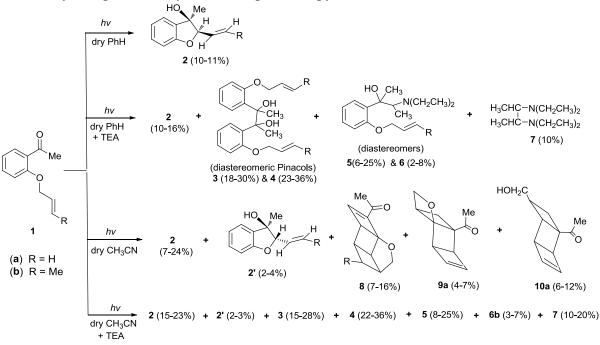
Photochemistry of carbonyl compounds has provided the chemists with a useful set of working and exemplar paradigms as carbonyl chromophore undergoes many interesting and versatile photochemical reactions. Consequently, photochemistry of carbonyl compounds has received more attention than any other single class of organic compounds. Photochemical transformations of saturated carbonyl compounds/conjugated carbonyl compounds and their mechanistic details have extensively been explored for the past three to four decades, however, the photochemistry of conjugated carbonyl compounds still continues to be the area of intense activity. We have investigated the photochemistry of some conjugated carbonyl compounds for understanding the nature of phototransformations involved, their mechanistic details, and development of new photochemical synthetic pathways.

Photochemistry of *o*-alkoxyphenyl ketones has been explored both mechanistically and for synthetic applications and has demonstrated that product profile/yields depend strongly on the solvent system, involved excited state $(n-\pi^* \text{ or } \pi-\pi^*)$ and conformational preferences. A plausible role of electron transfer component has also been invoked in cyclization of 1,5-biradical intermediate to dihydrobenzofuranol products in these phototransformations¹.

In order to understand the above referred role of photoelectron transfer, first section of the dissertation has been devoted to the photochemistry of *o*-allyloxy-/crotyloxyacetophenones under varied conditions of irradiation (Pyrex-filter and under N₂ atmosphere), including solvents such as acetonitrile which is known to favour electron transfer and in the presence of triethylamine (TEA); the latter is well known to quench the photoexcited carbonyl function by charge/electron transfer. The phototransformations in presence of triethylamine were also of interest because it has been reported that radical anions generated from reduction of a photoexcited carbonyl function can be trapped intramolecularly by an olefinic moiety in a synthetically useful manner. We have attempted to characterize complete product profile, including some unusual intramolecular arene-olefin addition products obtained by the n- π^* excitation of the carbonyl function (Scheme 1)².

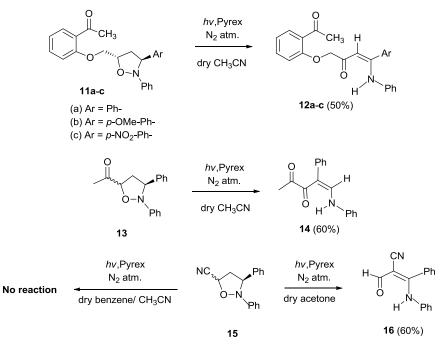
Irradiation of 1a,b in dry benzene led to the isolation of (syn)-2-ethenyl/propenyl-3-hydroxy-3-methyl-2,3-dihydrobenzofurans (2a,b) as the sole product. However, irradiation of 1a,b in dry benzene in the presence of triethylamine (0.1-0.4 mol equiv.) resulted in slightly increased formation of 2a,b, besides pinacols (3 and 4) and triethylamine addition products (5 and 6). Formation of 2a,b was suppressed with increasing molar ratios of triethylamine, with increased formation of products (3-7). On the other hand, irradiation of 1a,b in dry acetonitrile resulted in the formation of both syn-(2a,b) as well as *anti*-isomers of benzodihydrofuranols (2'a,b), besides some highly unexpected intramolecular arene-olefin addition products (8-10); formation of the intramolecular arene-olefin addition products was quenched in the presence of 0.1 mol equiv. of triethylamine. With increasing molar ratios of triethylamine in acetonitrile, formation of 2 and 2' was also suppressed with subsequent increased formation of products (3-7) derived from photoreduction of carbonyl function through electron transfer from TEA. No product derived from intramolecular interaction of the ketone derived anion radical/ketyl radical with an olefinic moiety was detected.

The intramolecular H-abstraction by photo-excited carbonyl followed by cyclization of 1,5biradical, which is an inefficient process in the case of o-alkenylmethoxyacetophenones, is slightly favoured in presence of lower molar equivalents of triethylamine and is quenched at higher concentrations. It has been proposed that the generally accepted limiting condition of a three-atom tether between an aryl ring and an alkene moiety for intramolecular photocycloaddition can be surpassed under the influence of polar interactions². These investigations have also led to the simple way of identifying diastereomeric pinacols derived from o-alkoxyacetophenones by ¹H NMR spectroscopy³.



Scheme 1

Second section of the thesis deals with the investigations on phototransformations of isoxazolidines. Although, there are few reports on the photochemical cleavage of isoxazolidine moiety⁴, however no report on the involvement of intramolecular photosensitization/photoelectron transfer/H-abstraction affecting such phototransformations is available. Guided by our earlier recorded observations on the role of electron transfer in the photochemistry of *o*-allyloxy/crotyloxyacetophenones², it was decided to explore the photochemistry of isoxazolidines sensitized by carbonyl functionality. Based on series of experiments, a useful methodology for the cleavage of an isoxazolidine moiety, which is generally known to be transparent under n- π^* excitation, has been developed⁵ (Scheme 2). It has been postulated that the facile photo-cleavage of isoxazolidines to β -enaminocarbonyl compounds (**12a-c**, **14**, **16**) is mediated by carbonyl functionality through the plausible involvement of intra- or inter-molecular electron transfer from nitrogen atom of the isoxazolidine moiety to photoexcited carbonyl function⁵.

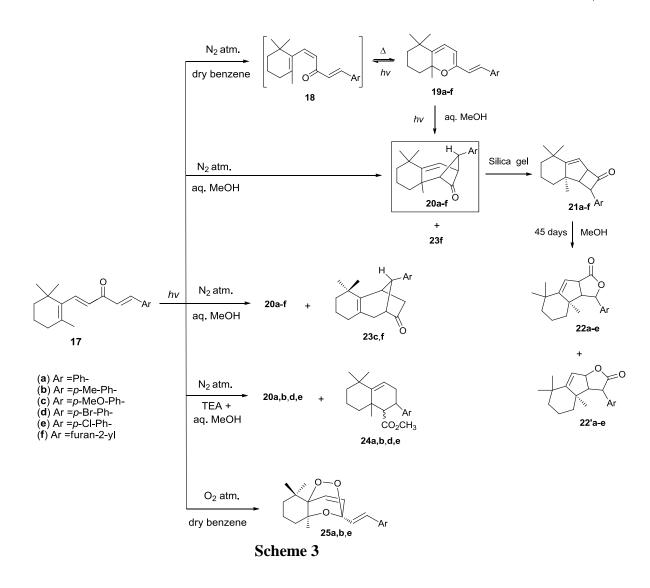


Scheme 2

Last section of thesis deals with the photochemistry of arylidene- β -ionones under varied irradiation conditions (Scheme 3, Pyrex-filter). It has been demonstrated that the irradiation of (E,E)-arylidene- β -ionones (**17a-f**) in anhydrous solvents afford 1,7,7-trimethyl-3-(E-2'arylethenyl)-2-oxabicyclo-[4.4.0]deca-3,5-dienes (19a-f) in high yields. Further irradiation of pure 19a-f in aqueous methanol resulted in Z, E-arylidene- β -ionones (18) through retroelectrocyclization, which underwent an intramolecular, exo-selective [4 **+** 21 photocycloaddition leading to 11-(*exo*)-aryl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-ene-3ones (20a-f, 60-80%) except in case of 19f, wherein formation of tricyclic ketones 23f was also observed. It is worth to mention that the tricyclic-butanones (20) rearranged over silica gel quantitatively to 5-aryl-7,11,11-trimethyl-tricyclo $[5.4.0.0^{3,6}]$ undec-1-ene-4-ones (21)⁶ and the latter underwent a facile unusual uncatalysed air oxidation to butyrolactones $(22 \& 22')^7$. A direct irradiation of **17a-f** in aqueous methanol led to **20a-f** (reduced yields compared to the irradiation of corresponding 19), along with the formation of novel tricyclic-ketones 23c (55%) and 23f (80%), in case of the irradiation of 17c,f. The tricyclic-ketones (23c,f) have been proposed to be derived from photodeconjugation in 18, followed by intramolecular [4 +

2] cycloaddition⁶.

In view of the known ability of triethylamine to quench triplet photoexcited ketones through charge transfer/electron transfer and speculated role of intramolecular photoelectron transfer in photo-conversion of arylidene- β -ionones (17) to tricyclic cyclobutanones (20)⁶, it was decided to carryout irradiation of arylidene- β -ionones in presence of triethylamine. Therefore, arylidene- β -ionones (17a,b,d,e) were irradiated in aqueous methanol in the presence of triethylamine (excess) to afford tricyclic-butanones (20a,b,d,e) along with bicyclic-esters (24a,b,d,e, ~20%, Scheme 3). Formation of 24 by the photochemical or thermal transformation of 20 was ruled out by the prolonged irradiation of 20e in aqueous methanol in presence of triethylamine (no phototransformation was observed) and by refluxing the solution of 20e in aqueous-methanol in presence of triethylamine for 4h (afforded 21e quantitatively). Further investigations will be necessary to unravel the mechanistic details of the phototransformation leading to 24.



In light of the reports that certain electron rich systems react with dioxygen without use of any singlet-oxygen-sensitizer to generate endoperoxides8a and known thermal routes to endoperoxides under electron-transfer conditions8b, it was decided to irradiate arylidene- β ionones under an oxygen atmosphere, to investigate the possible cycloaddition of electron rich conjugated- π system in 18 (generated in situ) with molecular oxygen under photoelectron-transfer conditions. Irradiation of arylidene- β -ionones (17a,b,e) in dry benzene under oxygen atmosphere afforded highly valuable stable endoperoxides (25a,b,e, Scheme 3) through the regio-selective [4+2] photo-addition of oxygen to a pyran in high yields (85-90%)9. It has been proposed that reaction occurs through an electron-transfer interaction between photoexcited 18 and molecular oxygen.

Investigations of the photochemistry of arylidene- β -ionones have provided an easy access to different tricyclic-butanones, stable endoperoxides and led to the discovery of an alternative mode of phototransformation to complex molecular frame-works such as tricyclic-ketones (23).

In conclusion, carbonyl chromophore has been crafted into different matrices for some unusual photo-transformations, utilizing some fundamental reactions such as H-abstraction, photo-electron transfer, cycloadditions and rearrangements, to develop new transformations of general interest and high synthetic significance.

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UV/Vis spectra database

UV/Vis⁺ Spectra Data Base (UV/Vis⁺ Photochemistry Database) <u>www.uv-spectra.de</u>

Andreas Noelle⁽¹⁾, Gerd K. Hartmann⁽¹⁾, F. Javier Martin-Torres⁽²⁾

⁽¹⁾ science-softCon, Maintal, Germany, ⁽²⁾ Centro de Astrobiología, Madrid, Spain

Introduction:

The science-softCon on-line "UV/Vis⁺ Spectra Data Base" is a not-for-profit project established in August 2000 and is operated in accordance to the "Open Access" definitions and regulations of the CSPR Assessment Panel on Scientific Data and Information (International Council for Science, 2004, ICSU Report of the CSPR Assessment Panel on Data and Information; ISBN 0-930357-60-4). The on-line database contains currently about 5,700 spectra (from low to very high resolution, at different temperatures and pressures) and data-sheets (metadata) of about 900 substances. In addition more than 250 links to on-line free available original publications are provided. The interdisciplinary of this photochemistry database provides a good interaction between different research areas. So, this database is an excellent tool for scientists who investigate in different fields such as physics and chemistry of planetary atmospheres, astrophysics, agriculture, analytical chemistry, environmental chemistry, medicine, remote sensing, etc.

Database content:

The on-line database comprises spectral data and information from EUV-VUV-UV-VIS-NIR spectral region. The database contains currently about 5,900 spectra/data-sheets (gas, liquid, solid phase, at low to very high resolution, and at different temperatures and pressures); and data-sheets (meta data: Publication, wavelength range, temperature, pressure, etc.) of about 900 substances and related photochemical information (quantum yields, photolysis studies, etc...). The database is open for new "Substance Groups" and additional spectra/data-sheets are being be added continuously. In addition more than 250 links to on-line free available original publications are provided. The database is subdivided into 27 substance groups. In addition to the substance group classification the user can search within CAS-list for the required spectral data and information.

Substance groups:

Alkali Compounds	Aromatic Compounds	Carbon Oxides	
Dyes	HalogenatedAlkanes, Alkenes	Halogenated Aromatics	
Halogenated Carbonyl Compounds	Halogenated Nitrogen Compounds	Halogens/Halogen Oxides	
Hydrocarbons	Hydrogenhalides/Hypohalides	Nitrogen Acids	
Nitrogen/Nitrogen Oxides	Noble Gases	Organic Acids/Esters	
Organic Carbonyl Compounds	Organic Nitrogen Compounds	Organic Peroxy Compounds	
Other Oxygenated Organics	Oxygen Hydrogen Compounds	PAHs	
PBDEs	PCDDs	Pesticides/Herbicides	
Radicals	Sulfur Compounds	Other Species (not yet categorized)	

All data-sheets (meta data) as well as the spectral data (2 column tables) are in plain ascii format. This allows an easy-to-use data handling without specific software requirements.

For some of the spectral data (e.g. for all dyes and several other substances) graphical representations (Fig. 1) are provided. It is intended to provide such graphs for all of the spectral data within the next months.

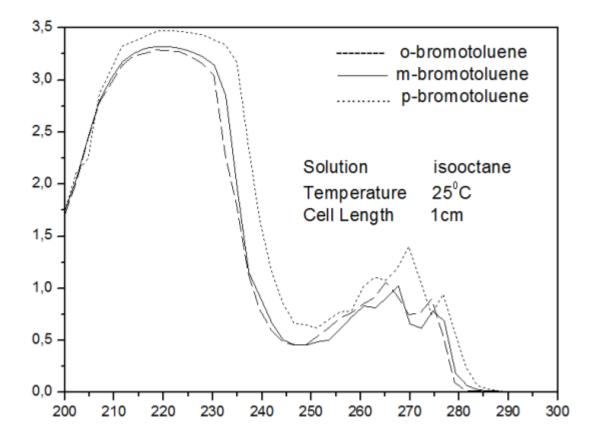


Fig. 1: Graphical representation of the UV absorption spectra of o-, m- and p-bromotoluene provided by Keli Han [1].

Preservation of spectral data and information

The *Committee on Scientific Planning and Review* (CSPR/ICSU) point out in his report "Scientific Data and Information" [2] that many important information gets lost due to technical forgetting. Many types of data are not being used for research because they are not available in digital formats. These data are in danger of being lost because the media on which they are recorded may decay (e.g., paper) or become corrupted (e.g., electronic media), or the software/hardware in which they are embedded may be superceded by new types of software/hardware. Often, the data are inadequately housed, catalogued, or preserved.

To avoid such technical forgetting the CODATA Working Group "UV/Vis⁺ Spectra Data Base" (2004-2008) recommended us to digitize spectral data and information (e.g. from graphical representations in published papers, especially from older publications) and provide these information via the "UV/Vis⁺ Spectra Data Base". We've started this very important but costly project in May 2010.

The aim of this project is to convert the graphical representations into digital tabulated spectral data. The accuracy of the digitized spectral information depends strongly on the quality of the graphical representation in the relevant publication. However, tests with

publications for which both the graphical representation of the spectra and the tabulated spectra are available showed that the error of the digitized spectra lies between 2 and 10 %.

Database quality assurance:

The database contains spectral data and photochemical information from published papers. To ensure the high quality standard of the fast growing "UV/Vis⁺ Spectra Data Base" an international Scientific Advisory Group (SAG) was established in 2004. The SAG members are in addition editors of the "UV/Vis⁺ Spectra Data Base" CD-ROM series.

Current SAG members:

Andreas Noelle	Gerd K. Hartmann	Askar Fahr		
science-softCon, DE	science-softCon, DE	Howard University, US		
David Lary	Stephane Le Calve	Paulo Limao-Vieira		
NASA-GSFC, US	CNRS, FR	New University Lisbon, PT		
F. Javier Martin-Torres	John J. Orlando	Farid Salama		
CAB, SP	UCAR, US	NASA Ames Research Center, US		
Ann Carine Vandaele	Richard P. Wayne	C.Y. Robert Wu		
BIRA-IASB, BE	University Oxford, UK	University Southern California, US		

In 2010 the on-line database celebrates the 10th anniversary. This was one reason for the SAG to establish an *Honorary Editorship* for the "UV/Vis⁺ Spectra Data Base" CD-Series. Starting with the 7th edition spectra CD (2010) the SAG nominates a scientist as *Honorary Editor* for each new spectra CD who had made significiant contributions in spectroscopy and/or photochemistry. For the 7th edition Prof. Johannes Orphal from Karlsruhe Institute of Technology (Germany) has been nominated and he has accepted his election.

Database access:

The on-line "UV/Vis⁺ Spectra Data Base" is sudivided into a "Literature Service" and a "Spectra Service". Via the "Literature Service" all datasheets (meta data) as well as many quantum yields and photochemical information are available free-of-charge for all interested users. In addition the "Literature Service" provides access to other related data like AutoChem software package (D. Lary, NASA-GSFC), Daily Solar Irradiances (J. Lean, NRL), MAS remote sensing data (G.K. Hartmann, MPAe) or Solar Ultraviolet Measurements of Emitted Radiation data (W. Curdt, MPS). The "Spectra Service" provides in addition full access to the digital spectra data. However, access to the "Spectra Service" but also to maintain the free-of-charge "Literature Service" and is in accordance to the "Open Access" definitions and regulations of ICSU/CODATA [2].

In addition to the on-line database science-softCon publish every 1-2 years a "UV/Vis⁺

Spectra Data Base" CD-ROM. The 7th edition [3] is a "mirror" of the on-line "UV/Vis⁺

Spectra Data Base" as of March 2010 and contains about 5600 spectra/datasheets of about

900 substances.

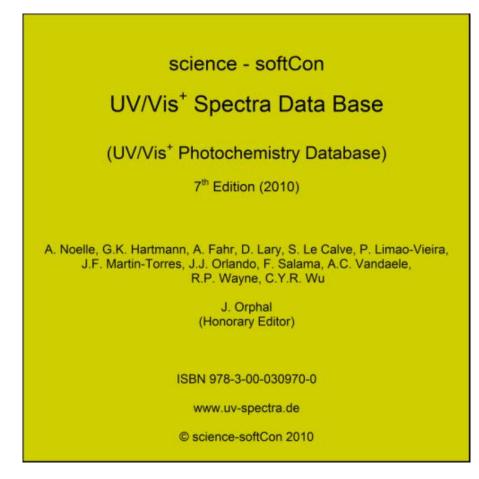


Fig. 2: Cover of the 7th edition "UV/Vis⁺ Spectra Data Base" CD-ROM [3].

Outlook:

The database is not static, additional spectra/datasheets and related photochemical

information (quantum yields, photolysis studies etc.) will be added continuously.

An application for a CODATA Task Group "UV/Vis⁺", as successor of the CODATA Working Group "UV/Vis⁺" (active from 2004-2008), to support the future development of the "UV/Vis⁺ Spectra Data Base" is envisaged. If you are interested in joining this initiative or if you have any questions/suggestions please contact us (<u>Helpdesk@science-softcon.de</u>). For more information see <u>www.uv-spectra.de</u>.

The support of the scientific community is crucial for such a data compilation project. So we would like to encourage the members of the scientific community to support this database.

science-softCon will provide a limited number of trial accesses to the on-line database for members of the *European Photochemistry Association* (EPA) who are willing to give us a short review for the database. If you are interested please contact our <u>helpdesk@science-softcon.de</u>.

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What Photochemists expect from Photochemistry

Collected by Davide Ravelli and Angelo Albini Dep. Organic Chemistry, University of Pavia via Taramelli 10, 27100 Pavia, Italy

Both Ciamician and Paternò credibly presented photochemistry as one of the leading disciplines for the role of chemistry in the developing society of their time. The visionary talk of the former scientist in 1912 included among the key topic the exploitment of solar radiation by storing it into small molecules of high energy. These would be used as fuel substituting fossil sources as energy vectors. Furthermore he foresaw new applications for materials ranging from photopolymers to photochromics.

Now that the science of photochemistry is well established, which are the next steps (or it is not, and a progress in basic science is urgently required)? Which new directions? How will be solar energy best exploited? In which way will photochemistry contribute to the make of better (more environmental-friendly) chemistry and to technological advancement in various fields, from energy to medicine?

Participants to the recent meeting 'Ciamician and Paternò Heritage - Photoscience a look into the future' were asked to give their answer to the questions above. As it appears from the following, practically everybody expects photochemistry to further develop as a source of *renewable energy* (particular important for developing countries), although there is some caveat about the troubles that the advancement in the field has encountered. Developing timeand space-resolved emission techniques should make possible biological studies at subcellular level and offer new *diagnostic* methods, and on the other hand insight into *individual* molecular properties should be offered by single molecule spectroscopy. And so on, in a quite optimistic mode. Photochemistry *is* the future.

Contributions

• BAGGALEY

Based on my relatively small experience of the photochemistry world to date, I would say that photochemistry applications in energy generation will be most promising and essential for the future, as coal and oil are finite sources of energy. Photochemical generation of energy, by way of mimicking photosynthesis in conjunction with new materials for energy storage, will be a good addition to range of sustainable energy already available. As research in this field is vast, I believe there is lots of scope for rapid development of this type of technology.

• BRASLAVSKY

Development of antennas mimicking natural antennas in photosynthetic organisms, this in connection with supramolecular structures

Using the knowledge acquired in the observation of naturally developed photosensors for the development of intelligent devices using different qualities of light (wavelength, intensity, direction) for the triggering of nanodevices and otherwise all types of devices

Detailed analysis of several light-induced natural processes in organisms. Understanding the light-triggered signals in all organisms, from achaeas to mammals

• BROUWER

As Ciamician already foresaw, but more than 100 years later, photochemistry will finally help to solve the energy supply problem by converting sunlight to fuels.

Rather than promising a development, it is important to point out the main requirements for photochemistry to be useful in technological contexts such as solar energy and light emitting diodes: we have to control the diversity of photochemical pathways, in particular find ways to avoid photodegradation.

Photochemical methods have found their way into many technologies, and this will continue. Exciting developments are in single molecule-based techniques, which allow the combination of imaging with chemical sensing. Whether it will be really useful or not is hard to tell, but single-molecule studies of chemical reactivity are very exciting. Great progress has been made and will continue to be made in computation-based theoretical modeling of excited state dynamics.

• BURROWS

One area in which Ciamician showed the potential of photochemistry and in which it is going to play a major role in this century is in helping to resolve the energy problem through solar energy conversion, either into electrical energy or into chemicals, such as molecular hydrogen. Although there are existing and efficient inorganic semiconductor systems, organic and polymer based ones are becoming of increasing importance and will play a major role.

A second major area involves electroluminescent light emitting organic and polymeric systems. In the near future these will be of increasing importance in general illumination, and may lead to major changes in the way we think about architecture and design.

A third area is the link between photochemistry and biology, and in particular the development of luminescent and other photophysical probes for both sensing and imaging processes at the cellular and subcellular level. There are already a number of interesting studies in this area, but I think they will develop rapidly in the very near future in terms of both spatial and temporal resolution. This will have implications on both understanding biological processes and also for clinical diagnosis, both in hospitals and at home.

• CALOGERO

In my opinion the most promising developments of photochemistry in the near future are:

- 1) photocatalysis for destruction and reduction of pollutant
- 2) photoenergy conversion
- 3) photoluminescent sensor
- 4) photo-therapy

in combination with nanotechnology, optics, photobiology, ecc...

• CERONI

Finding solutions to the energy problem by developing solar cells and artificial photosynthesis

• COCCHI

Green Photonic like optoelectronic devices based on organic materials: High efficient solid state lighting (OLED) Photovoltaic Cells

• CREDI

The most important task of photochemistry in the (near) future is the identification of viable strategies for converting sunlight energy into fuels. Progress in photovoltaic conversion, in my opinion, is in the hands of materials scientists more than in those of photochemists. Another important objective is to make photoactive (nano)materials and (nano)devices for advanced applications in a variety of fields ranging from information processing, catalysis, environmental control and cleaning, diagnostics and medicine.

• DE SCHRYVER

Inorganic photovoltaics OLED's Subdifraction imaging fluorescence microscopyin material science and in bioscience

• DONGHO KIM

I'd like to recommend the two topics; one is Multidimensional Vibrational and Electronic Spectroscopy and the other one is Single Molecule Spectroscopy. The former provides indepth information on molecular dynamics involved in energy relaxation processes and the latter gives insight into individual molecular properties hidden in ensemble measurements.

• FAGNONI

Green Chemistry for sustainable development.

• FASANI

Photochemistry is actually a multifaced science that is spread in a lot of research fields. In my opinion an excellent development for the future should be towards applications exploiting the energy of light for environmental protection and improvement of health.

• GHIGGINO

Photochemistry is continuing to evolve into a multidisciplinary subject that encompasses the physical and life sciences and engineering. At the fundamental level the technical ability to observe photochemistry and photophysics of single molecules in condensed phases will drive our understanding of the distribution of behaviours that make up bulk photochemical properties, and enable an insight into the photochemistry of molecules in living cells. One can expect new theoretical and experimental approaches to reveal the diversity and consequences of quantum effects on energy transfer and other photochemical processes in complex biological and macromolecular systems. Finally in the near future we can expect photochemists to make major new contributions to addressing sustainable energy issues through the development of new materials and new understandings for photovoltaic solar cell design.

• GUSTAVSSON

Being a spectroscopist, I think of multi-dimensional spectroscopy and/or IR-spectroscopy. To follow the reorganisation of intramolecular chemical bonds remains a challenge, but people like Hochstrasser in the US and Peter Hamm in Europe have shown the feasibility.

Also, coherent phenomena and/or coherent control is getting more and more promising, particularly in biological systems. People like Jenifer Herek in Europe show the way.

• ISHITANI

It should be conversion of solar energy to both chemical and electrical energy. Although this is a very old research field, we have been able to give useful technologies to the public because of various difficulties. However, these technologies will be crucial for all human beings in future. There are still many things to be pursued by photochemists.

• KARPIUK

Better understanding of the relationship between the chromophore structure and the photophysics and photochemistry of organic molecules, including that on submolecular but also on topological levels will lead to the development of novel, highly efficient, stable fluorophores with specific properties tailored for various applications, including, for instance, solid state lighting or high resolution fluorescence microscopy. This development, coupled with OLED technology is likely to have an substantial impact on the everydays life of our civilisation within the next 20 years. The research on structure-property relationships is a very important aspect of the development that has somehow been shadowed recently due to enhanced focus on the material side.

A substantially deeper insight into the photophysics of molecular systems will be gained in line with the development of femtochemistry and studies on intramolecular dynamics in the time scale of molecular vibrations, especially in application to larger molecules.

The work on photocatalytic decomposition of water and generation of hydrogen as an ultimate "pure" chemical fuel will finally bring a breakdown in gaining the energy from the sun for transport, heating and electricity. Given the advances up to now, one should be, however, careful in assessing the perspective.

The history of modern photochemistry is slightly longer than one century, which virtually means four – five generations of photochemists. Given the splendid achievements of our predecessors, some of which had to carry out photochemical reactions not with lamps but with sunlight, not to mention simple tools and instruments of the past, we can only optimistically look forward to what the present and future generations will add to the growing edifice of photochemistry.

• KNOER

The role of photochemistry as a versatile tool for triggering, driving and controlling molecular processes at the speed of light will further increase enormously and reach a deep level of cross-disciplinary applications all over the natural sciences and beyond!

Certainly photo-assisted processes will continue to play a crucial function in the context of solar energy utilization for artificial photosynthetic syntheses of fuels or other useful materials in sustainable and environmentally benign "green" processes, as already visioned by Giacomo Ciamician. In general, there is currently a clear switch from trying to break bonds with light to efficiently forming new bonds with photochemical and photocatalytic

tools. At the moment, asymmetric photocatalysis remains an important benchmark to be reached.

Photochemical key-steps definitely will further conquer the life and material sciences. The light-triggered formation of structures, release or deposition of materials by photonic techniques is already present allover the field. In the life sciences, besides innovations in "molecular photomedicine", the utilization of photons as a source of energy and moreover as a bit of information will probably make the fastest conceptual progress in the near future. About a decade ago, we introduced the field of biomimetic and bio-inspired photocatalysis as a new branch of photochemical research. This novel field is now starting to become generally accepted and will rapidly mature. The first monography on "Bioinorganic Photochemistry" published this year (to speak in the sense of Kuhn's "Structure of Scientific Revolutions") may be taken as a first clear sign for this effect.

One of the most "exciting" potential applications of excited state processes in the life sciences is the remote control of intracellular processes within living organisms by introducing photoswitchable and light responsive small molecular compounds. If research in this direction will succeed, this will certainly open completely new possibilities with long-ranging implications in biology, medicine and neurosciences among others.

So, already now, a broad scientific community has become aware of the many advantages of involving photochemical key-steps in their research in order to solve demanding scientific problems in a creative and efficient way! In this context, it will be one of the most important roles of photochemists to further distribute a profound knowledge about the fundamentals and basic concepts that have evolved since Ciamician, Paternò and others started to define the field. This also includes a critical assessment of experimental details, methods applied and conclusions drawn to assure a certain level of quality and reliability of photochemistry related scientific output.

• KONDRIATIUK

From the very beginning photochemistry was inspired by nature in its wonderful ability to employ light for formation of chemical bonds in photosynthetic bacteria and therefore the most promising development of photochemistry in the future will be if we learn how to realize the same process artificially and as efficiently as it does nature.

• LAINE

This is our duty and well-understood interest to supplement Nature so as to ensure the perpetuation of the human race. Clearly, supplying to our ever increasing demand of resources on board of space-ship Earth must go through reinforcing the coupling between our planet and the sun, viewed as an the infinite source of power/energy. As a matter of fact, also, the molecular scale is the scale of Nature at work, and is therefore the most relevant level for a bio-compatible human intervention, provided that abundant and non-toxic elements are used. To obtain such nanometer-scale factories functioning as tiny photo-reactors converting sunlight energy into storage chemicals (fuel), there must be a spatiotemporal control of multiphoton / multi-electron processes. Within this framework, the design of photochemical (supra)molecular devices able to –temporarily– storing electronic excitations (i.e. energy) would constitute, for instance, a critical step. If Supramolecular Chemistry provides with the most efficient tools to produce complex integrated multifunctional supermolecules, the bio-inspired conceptual corpus of Supramolecular Photochemistry, put into words by Balzani, appears as the most promising means to bring back a little to Nature and to supplement It to solve our problem of global warming, towards the goal of powering the planet.

• LANDGRAF

Theory:

Complete integration of Marcus theory into photochemical quenching processes. Better understanding of these reactions.

Experiment:

Combination of photochemistry with magnetic field. Studying magnetic field sensitive processes under strict control of all other parameters, such as temperature, polarity, viscosity, refractive index, etc.

Application:

Further integration of semiconductor light sources into known techniques in order to make them available for a larger community.

• LEMMETYINEN

The greatest challenge facing our global future is energy. Rising living standards of a growing world population will cause global energy consumption to increase dramatically over the next half century. Within our lifetimes, energy consumption will increase at least two-fold. The challenge for science is to meet this energy need in a secure, sustainable, and environmentally responsible way. The additional energy needed for 2030 - 2040 over the current energy base is simply not attainable from long discussed sources, including nuclear, biomass, wind, geothermal, and hydroelectric. The global appetite for energy is simply too much. The environmental and global security reasons dictate that growing energy consumption needs to be met by renewable and sustainable sources.

Of the possible sustainable and renewable carbon-neutral energy sources, sunlight is preeminent. The sun is emitting to the surface of the earth every 60 minutes the amount of energy corresponding to the increased annual energy consumption in 2040. If photosynthesis can be duplicated outside the leaf - artificial photosynthesis - the sun's energy can be harnessed as a fuel.

For the reasons described above the impact the research of hundreds research groups, on the societal development of the humanity is undeniable.

• MANET

I remember G. Ciamician telling that light would have been the problem to solve the energy problem in the future. Several decades have past ignoring his message mainly due to the abundance of petroleum easily gained. Only the last decades more scientist have got interested in the problem. The development of cheap flexible solar panels made of material that can easily be obtained would certainly represent a revolution for our civilisation and open to a more equal distribution of welfare. Thinking of third world countries the discovery of natural compounds to be extracted from local vegetation and working as antennas in solar panels or exhibiting light induced properties of interest also in other fields would represent an opportunity to create locally new enterprises improving at the same time everyday life. In this frame researchers of industrialised countries should look for collaborations with researchers of third world countries in order to pass their knowledge and allow them to play a role as teacher and innovator in their country of origin.

• MANFRIN

Nano-particles, sensors and Solar panel applications.

• MARKOVITSI

A promising development concerns the processes occurring in DNA following absorption of UV radiation. This is important in various respects:

- 1. The description of the excited state dynamics of the monomeric DNA/RNA chromophores (bases, nucleosides, nucleotides) and the way that it is affected by environmental factors will help understanding their "selection" as building blocks of life.
- 2. Elucidation of the photoprocesses in double helices will provide information about the initial steps triggering a cascade of events that ultimately lead to skin cancer. Although many photoproducts have been isolated, the primary processes preceding their formation as well as the associated time-constants and reaction intermediates remain unknown. The first time-resolved study describing the formation of a photoproduct within a single strand appeared only in 2005. So far, no such studies have been performed for a double helix.
- 3. The use of DNA components as building blocks in non-conventional materials for applications in molecular electronics and optoelectronics is a rapidly emerging field. The most representative example is provided by guanines due to their ability to self-assemble into nanoscale structures, including long nanowires. It is worth-noticing that there is presently a European COST Action on this topic (<u>http://www.g4net.org/</u>). The characterization of the electronic excited states is a prerequisite for integration of such systems in electronic devices.

The first spectroscopic studies on DNA appeared about half a century ago. For long, these studies were limited by the time-resolution necessary for the study of the singlet excited states of DNA components. During the past decade, the development of appropriate femtosecond techniques and computational methods gave rise to an intense activity in this. Beyond the determination of the lifetimes of singlet excited lifetimes of the bases, the recent studies revealed unexpected aspects and put forward new challenges. I cite a few of them:

- What are the photoprocesses induced by UVA photons which are more abundant in the solar spectrum reaching the earth compared to UVB or UVC photons? It was shown recently (2010) that although the monomeric DNA chromophores do not absorb in the UVA spectral domain (320-400 nm), double strands do. As a consequence, thymine cyclobutane dimers, which constitute the major DNA lesion, are formed.
- How oxidative damage induced by photon absorption varies with the wavelength, the base sequence? What are the precise photoreactions?
- How photoprocesses in double helices are affected by cytosine méthylation which is natural process? Only 2% of the cytosines are methylated whereas 40% of them are involved in carcinogenic mutations.
- On more fundamental grounds, how conformational dynamics of the double helix affects trapping and detrapping of the excitation energy and contributes to overcome energy barriers related to photochemical reactions?

Answering these questions is quite important for the post-genomic era.

• MASUHARA

Which is the most promising is difficult to answer, but the followings will be hopefully one of the interesting topics in molecular photoscience.

Laser trapping chemistry

The focused intense CW near IR laser beam exerts mechanical force on molecular clusters, polymers, nanoparticles, and so on in solution at room temperature and gathers them at the focal point. This laser trapping is usually difficult for single molecules, while 2 possible enhancement effects are considered to be effective for enhancing laser trapping. One is to introduce the second visible laser beam, which wavelength matches with the electronic absorption of the target molecule, in addition to the trapping laser, and this is called "resonance effect". The second effect is ascribed to surface and interface of solution, which will be due to characteristics 2-dimensional structure and dynamics and can be called "interface effect".

The interface effect has recently enabled us to realize Laser Trapping Crystallization for the first time. The resonance effect, maybe coupled with the interface effect, will realize single molecule spectroscopy and photochemistry in solution at room temperature. More probably a demonstration will be given for local polymerization where gathered monomers at interface undergo reactions efficiently.

• MISAWA

My recent research interest is the creation of spatially amplified field regions by localization of photons in specially designed micro- and nano-structures, where photochemical interactions can be promoted to the rates substantially exceeding those found in bulk homogeneous materials. For this purpose, a research group (Grant-in-Aid for Scientific Research (KAKENHI) on Priority Area (2007-2010), MEXT, Japan) was constructed three years ago. The research theme in the priority area was named as "Strong Photon-Molecule Coupling Fields for Chemical Reactions". Proper theoretical understanding of optical interactions between phtons and molecules/materials occupying the strong, localized field regions needs to be developed, indicating the possibility of achieving novel photochemical reactions. These expectations are being studied by experimental approaches, for example, multiphoton excitation localized within spatial domains as small as single nanometer region. In order to better exploit these results, special collaborative initiatives along the lines of "nanoengineering" and "light energy conversion device structuring" was set up.

According to these background, we have recently constructed plasmonic photoelectric conversion systems from ultraviolet to near-infrared wavelength without deteriorating photoelectric conversion by using electrodes in which gold nanorods (Au-NRs, 240 x 110 x 40 nm^3) are elaborately arrayed on the surface of n-type TiO₂ (0.05 wt % of Nb-doped) single crystal electrodes. The development of a high-efficiency solar cell is critical in order to create a future realizing low-carbon society. To produce a solar cell with high photoelectric conversion efficiency, we need to develop a system that responds to wide spectrum of solar light, from ultraviolet to near-infrared wavelength. However, the spectral distribution observed on earth in the infrared wavelength region longer than 800 nm accounts for 41% of the entire solar energy, and only a few solar cells can efficiently convert solar energy with such a long wavelength to electrical energy. This system can be also applied to transparent solar cell working at near-infrared wavelength and can be used for solar cell which can set in living body.

• MURAKOSHI

Importance on Plasmonic Photochemistry: Light-matter interactions are not efficient on a single molecule scale; indeed, statistically it requires 10 millions of molecules should be encountered for a single photon to be absorbed. The aim of this research is to study photochemical reactions at the single molecular level and make the most efficient use of

photons. If we utilize a metallic nano-structure that interacts with photons and allows energy localization within a space of nanometers in cross section, it would be possible for a single molecule to be excited by a single photon. This would correspond to the extension of absorption cross-section of molecules.

Surface plasmons localized on metallic nanoparticles and metallic nano-structures can have strength of their electric field enhanced by a factor of 10^5 - 10^6 as compared with that of the incident light. In photonic crystals, enhanced light-matter infractions may be achieved by engineering of photonic band dispersion properties and slowing the light. Under these circumstances, it is highly probable that the selection rules in photon excitation are changed for the molecules exposed to extremely strong electric field gradient when wave function of a molecule is nearly overlapping with the distribution of electromagnetic field localized within the same nanospace.

By utilizing metal nano-structures and photonic crystals non-linear optical phenomena like two-photon absorption can be induced using low intensity light, although observation of twophoton absorption conventionally requires irradiation by intense ultra short pulse lasers.

• NAU

I think with respect to practical applications, the field of fluorescence is by far the dominant one, reaching from sensing and extending to information storage. The next generation of data storage devices will for sure be based on fluorescence read-out.

The area of solar energy conversion is another ever-lasting strength of photochemistry, but unfortunately is dominated by minor technical advancements, form a chemical point of view perhaps molecules with improved charge recombination characteristics. Nevertheless, the concept is well worked out and any improvements in this field can only be minor in nature.

Smart photochemical materials capable of switching as well as LCD displays are another promising area, with photochromic materials clearly taking a lead. This provides many challenges also to (synthetic) chemists.

• OTTO

There are several promising areas of photochemistry, in which we can expect significant developments in the near future. One of them is photocatalytic water-splitting producing hydrogen by utilization of solar energy in the near UV and visible range. Through such a procedure the most abundant renewable energy could be converted into the cleanest fuel. Although thermodynamically several systems looked appropriate in this respect, no really efficient one has been compiled so far. The requirements of the sustainable development, however, will urge us to find a reliably operating system, and I do believe it will be managed.

• OTTOSSON

Investigations and applications of excited state aromaticity.

Beside the obvious and important developments in the applied areas of photochemistry, e.g., to deduce how one efficiently converts solar irradiation into electricity and fuels, I would like to stress a more fundamental field of photochemistry that I believe will see a revival. Namely, the study of how aromaticity influences different photochemical and photophysical properties. The rule for aromaticity in the lowest triplet $\pi\pi^*$ state was published by N. Colin Baird in 1972 in a paper named "Quantum Organic Photochemistry. II. Resonance and Aromaticity in the Lowest ³ $\pi\pi^*$ State of Cyclic Hydrocarbons" (*J. Am. Chem. Soc.* **1972**, *94*, 4941). Even though aromaticity is a central concept to ground state (organic) chemistry, it is

still exceptionally seldom applied to rationalize excited state properties and processes of organic compounds.

Recently, several papers have appeared that indicate that Baird's rule on triplet state aromaticity is not only applicable to the lowest triplet state of annulenes, but it is also valid to the lowest singlet excited state of such compounds. Thus, the concept of excited state aromaticity should be a general and widely useful tool for rationalization of excited state properties and processes of conjugated molecules. It could possibly also serve as a tool for design of compounds with targeted optical properties, and it could open up for new and more efficient reactions in synthetic organic photochemistry (or for improved understanding of existing ones).

Conclusively, I think (and hope) that the fundamental research area of excited state aromaticity is one area of photochemistry that will see significant future development.

• PHILLIPS

Solar energy conversion is increasingly crucial if society is to thrive in a post-hydrocarbon world.

The continued expansion of photodynamic therapy and other applications of light in medicine will play a role.

Control of photochemical reactions using pulsed lasers remains a goal, probably never of commercial interest, but of great theoretical importance

• PRODI

Development of photoactive structure for medical diagnostics and therapy

• RICHERT

Given the current energy situation, including the depletion of natural resources, topics tending towards energy conversion, energy storage, and energy transfer will certainly be relevant in the near future. This covers a wide field of research where fundamental research dealing with photoinduced energy transfer and charge separation is certainly as important as applied research where the work is accomplished in direct cooperation with industry.

Another important aspect is the development of novel techniques and strategies for the clarification of chemical reaction mechanisms. Such studies allow gaining more insight into the elementary physical processes and are essential, because without this insight, trying to understand the complex biological processes that came more and more into focus during the last few years will result in mere speculations. Therefore, the importance of the study of model systems, even if sometimes not directly linked to any application, should not be underestimated.

• SALTIEL

The use of solar energy in meeting, in part, society's energy needs.

• SAMPEDRO

In my opinion, the main contribution of photochemistry to the science in general and the society as a whole will come from the solar energy exploitation. In these days of such a high

energy demand and with the shadow of fossil fuel shortage approaching, rational and effective use of solar energy could help to maintain our present economic growth.

Besides, photochemistry should definitely play a major role in the development of "green" organic processes and transformations.

Underneath these two main contributions, photochemists should gather together more information on the molecular basis of photochemical reactions. Collaborations between experimentalists and theoreticians will be here crucial.

• SCHANZE

Solar energy conversion of light into electricity or fuels.

Photochemistry and photophysics as a tool in biology and materials science, e.g., development of imaging probes and sensors based on fluorescent signalling

• SEBEJ

I will not try to emphasize the importance of solar energy and the technology behind, because the photoremovable protecting groups (ppg) is the area I am working in. Not being the most important nor promising one to the future applications, it is offering a wide variety of application in organic synthesis, lithography or combinatorial chemistry. But the further implications of ppg and related chromophores to the area of molecular biology and cell biology (and even medicine) seems very promising by offering precisely time and space limited tool for study of cell processes. Also the photo-medicine is the area of interest, with new discoveries about the photo-induced bonding of tissues in addition to photodynamic therapy.

• VENTURA

In my opinion solar energy conversion within the perspective of fuels production is one of the most promising developments of photochemistry, that could be helpful in facing the task of global energy crisis.

Another important development useful in medical technology is the photoinduced death of cancer cells achieved by means of suitable photosensitizers. The recent introduction of two photon excitation that permits a deeper treatment of living tissues is of great interest.

• VENTURI

In the field of energy for the development of artificial photosynthesis. Conversion of solar energy into fuel by artificial photosynthetic systems is certainly one of the most challenging goals in chemistry. If chemists will succeed to create an artificial photosynthetic process, "… *life and civilization will continue as long as the sun shines!*", as the Italian scientist Giacomo Ciamician forecast almost one hundred years ago.

In the field of nanotechnology. Indeed, if and when a nanotechnology-based industry will be developed, its products will have to be powered by renewable energy sources, because it has become clear that the problem of energy supply is a crucial one for human civilization for the years ahead.

• VON ESCHWEGE

I believe the Photochemistry of the future lies mainly in the field of new opto-electronics, with specific developments in the field of larger molecules and its potential role here. Unlike previous and existing electronics, involvement of large organo and/or metallic complexes have almost endless "handles" for molecular engineering – towards required goals. These developments are expected to go hand-in-hand with new photochemical energy conversion technologies, e.g. photo-voltaic cells with comparisons to photosynthesis.

- WEINSTEIN
- Fundamental understanding of photosynthesis.
- Development of ultrafast spectroscopic methods including imaging on the nanoscale.
- Development of multidimensional correlation methods such as 2D-IR spectroscopy to understand presently unknown mechanisms of vibrational coupling in electron and energy transfer processes in small molecules, extended assemblies, and materials.
- Fundamental understanding of electron and energy transfer based on the above.
- Based on the above, development of a plethora of efficient artificial systems for solar energy capture, storage, and controlled release, and for photocatalytic use of solar energy.
- Development of efficient emitting materials.
- Finally, it is important to stress that only combined efforts of scientists from different disciplines can bring about the success of the key direction above.
 - ZACHARIASSE

To obtain a detailed analysis in time (femtosecond) and spectral resolution of photochemical reactions

Ciamician – Paternò Heritage Photosciences a look into the future Ferrara (Italy), Aula Magna del Rettorato, July 16-17, 2010

The international Ciamican - Paternò meeting drew inspiration from the legacy of Giacomo Ciamician and Emanuele Paternò, who, between the end of 1800 and the beginning of 1900, have been the two leading figures of the Italian chemistry. Both associated with Stanislao Cannizzaro, they had an important role in the development of Chemistry in Italy, with the establishment of the Italian Chemical Society (SCI), the national chemistry journal "Gazzetta Chimica Italiana", and the participation to international scientific activities. Although interested in various aspects of chemistry, they gave a dramatic contribution to the field of photochemistry and, therefore, can be considered the founders of this discipline. As in 1910 they documented a large number of key processes in organic photochemistry, *we can conclude that 2010 constitutes the 100th birthday of photochemistry*.

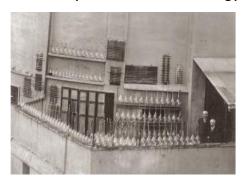
The meeting started in Ferrara (Italy) in the afternoon of Friday, July 16, 2010, immediately after the conclusion of the XXIII IUPAC Symposium on Photochemistry, which took place in the same city from 11 to 16 July, 2010. This half day was dedicated to an exhibition of posters and documents dedicated to Ciamician and Paternò, the giant pioneers of Photochemistry. The exhibition, located in the main hall of the University of Ferrara's Rettorato (Palazzo Renata di Francia), was aimed at showing not only the development of photochemistry in the Ciamician's and Paternò's laboratories, but also the importance of the studies, ideas, and predictions of these two scientists for the growth of photochemistry as a mature discipline.

At the end of the day, before the get together party, a welcome address was given by Luigi Campanella (President of the Italian Chemical Society), H. Inoue (President of the Asian & Oceanian Photochemistry Association), D. Markovitsi (President of the European Photochemistry Association), and K. Schanze (President of the Interamerican Photochemical Association).

The day after, July 17, worldwide famous scientists contributed to illustrate the future trends of photochemistry with lectures, each devoted to a specific aspect of this rich and multi-faced research field.

Daniel G. Nocera of the MIT of Cambridge (USA), referring to the well known Ciamician's conference "The photochemistry of the future", made a glance to the most important and compelling challenge: the creation of new compounds and "*the photochemical processes that hitherto have been the guarded secrets of the plants*". He illustrated the behaviour of a new cobalt oxygen-evolving catalyst that, as the Oxygen Evolving Complex of plants, is self-repairing, self-assembles upon a one-electron oxidation of an earth abundant metal, and is comprised of a partial metal-oxo cube; this structure is very important, both in the artificial and natural system, for accomplishing the water splitting reaction. As Nocera pointed out, such a catalyst is well-adapted to provide distributed solar energy, especially to the poor.

Ciamician pioneer of solar energy



Ciamician and Silber in their laboratory balcony

"In the desert regions, unadapted to any kind of cultivation ... forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry, which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization based on coal, shall be followed by a quieter civilization of solar energy, that will not be harmful to progress and to

human happiness."

G. Ciamician, Science, 1912, 36, 385

Paternò pioneer of organic photochemistry



The Paternò's cabinet

"It is well known from the most remote ancient times that life meets solar energy, light and heat; we can find several and sure signs in the work of writers and poets in every epoch. However, our aim is not to be interested in the action of light in the organic evolution and in life, but we want to look into the action of light on the phenomena attributable to the chemical affinity, combinations, and decompositions. ... in the laboratories and in the factories, who uses light? Perhaps a reason of this situation is due to the fact that several reactions performed by using light occur also and more rapidly by using heat and to the belief that the similarity between the action of light and heat is greater than it actually is. ...until now the chemists did not got from such a potent agent, as solar light is, all the benefits that undoubtedly it will be able to give"

E. Paternò, Gazz. Chim. Ital., 1909, 39, 237

The lectures of the subsequent invited speakers described the most recent results dealing with a) the photoinduced geometrical structure changes of molecules in densely packed crystals (Masahiro Irie, Rikko University, Tokio, Japan); b) the role of entropy to control the outcome of photochemical events (Miguel A. Garcia-Garibay, University of California, Los Angeles, USA); c) the behaviour of singlet oxygen that will remain at the forefront of science exhibiting always new aspects and surprising properties (Peter R. Ogilby, Aarhus University, Denmark); d) the conical interactions as a common mechanistic entity for the discussion of both light- energy wastage and light-energy exploitation at the molecular level (Massimo Olivucci, University of Siena, Italy); and e) the effects of light on human health and in medicine (David Phillips, Imperial College, London, UK).

The meeting was closed by the lecture of Vincenzo Balzani (University of Bologna, Italy). He draw the attention of the audience on the hot topic of artificial molecular devices and machines, with the aim to answer one of Ciamician's questions: "Is fossil solar energy the only one that may be used in modern life and civilization?". According to the speaker, exploitation of non fossil solar energy is the only possibility of overcoming the current energy and climate crisis. A novel way, perhaps not the most straightforward one, is to explore the utilization of sunlight in the creation of artificial devices and machines. The creation of these artificial photochemical devices is of interest not only for expanding the field of photochemistry, but also for the growth of nanoscience and the development of nanotechnology. Recent developments in such a field have opened several avenues to frontline scientific research, like for example (i) the possibility of processing complex

information inputs/outputs by very simple molecular and supramolecular compounds, with the goal to construct photonic molecular computers, and (ii) the exploitation of photoinduced motion at the molecular level to directly convert sunlight into mechanical energy. This lecture clearly showed that the interaction of light with matter is an important process not only for the progress of science, but also for the progress of mankind.

At the Ciamician and Paterno's time photochemistry was thought of as one of the "sciences of the future", expected to have a major role in the economical and scientific progress. The lectures presented at this meeting showed that in a hundred years photochemistry has satisfied most of the expectations, but it is still a science of the future: photochemistry will be indeed greatly involved in solving the growing needs of modern society in a clean way and mild conditions.

To conclude we would like to thank Prof. Angelo Albini and his Group of the University of Pavia (Italy) for the accurate organization and the success of the meeting.

Maria Teresa Gandolfi and Margherita Venturi Department of Chemistry "G. Ciamician" – University of Bologna (Italy)

X Encuentro Latinoamericano de Fotoquímica (X ELAFOT) X Latin-American Encounter on Photochemistry La Serena, Chile, October 10-14, 2010

The Conference was scheduled for April 2010, but due to the consequences of the devastating February earthquake and tsunami, the Conference was postponed. The Chilean colleagues (especially Elsa Abuin and Antonio Zanocco) should be strongly congratulated, because they managed to put together an excellent program and to reschedule the meeting for October in the same place as originally planned.

There were 182 participants (some, but not all, are in the picture below), from which 85 were students. The participants were mainly from Chile, Brasil, and Argentina, as well as some from Colombia, 4 from Russia and three from Germany. Due to the rescheduling, there were very few "gringoes". Prominent among them were Ana Moore, Gonzalo Cosa, Susana Sánchez, and myself. It is always a great pleasure for those Latin-Americans working abroad to go back to our lands and witness the enthusiasm and engagement of the young people in our home Countries, as well as to establish working ties with the research groups.

The plenary lectures by Ana Moore (Arizona State Univ.), René Nome (Univ. São Carlos and UNICAMP), Susana Sánchez (Univ. California, Irvine), Pedro Aramendía (Univ. Buenos Aires), Teresa Atvars (UNICAMP), Gonzalo Cosa (Univ. Montreal), Andrés Thomas (INIFTA, La Plata), and Silvia Braslavsky (Max-Planck-Inst. for Bioinorg. Chem., Mülheim an der Ruhr) handled a variety of subjects, from the mimicking of natural photosynthesis for solar energy use, single-molecule spectroscopy, photopolymerization, calculations and complexes spectroscopies, to photo-sensitizations and the solvent influence in photoreactions. The invited lectures were mostly given by very engaged younger researchers. The discussions were very lively, as well as the poster sessions in which 160 posters were wonderfully presented in two afternoon sessions.

There was a session dedicated to Carlos Previtali, leader of the photochemistry group at the University of Rio Cuarto (Argentina) and teacher of several generations of photochemists and another dedicated to Eduardo Silva (Universidad Católica de Chile) who has established an internationally recognized research group on flavins and their photoexcited chemistry. The venue was excellent and we could only complain about the weather, which was rather cold (bad luck !). The Conference excursion was to the very picturesque Elqui Valley, including a visit to a Pisco-making Cellar with the corresponding wineyards, and to the town where Gabriela Mistral (1945 Chilean Literature Nobel Prize) was born. We all shared the happiness of the Chilean colleagues for the rescue of the 33 miners, which happened during the Conference and we also shared the Thursday after-dinner dancing, which, as is a habit in these Conferences, was very lively.

The next ELAFOT will most probably be in Argentina in 2012, and we hope to meet again earlier, during the Inter-American Photochemistry meeting to be held in Mendoza in May 2011.

Silvia E. Braslavsky Max-Planck-Institute for Bioinorganic Chemistry (Formerly Radiation Chemistry) Postfach 10 13 65, Mülheim an der Ruhr, Germany

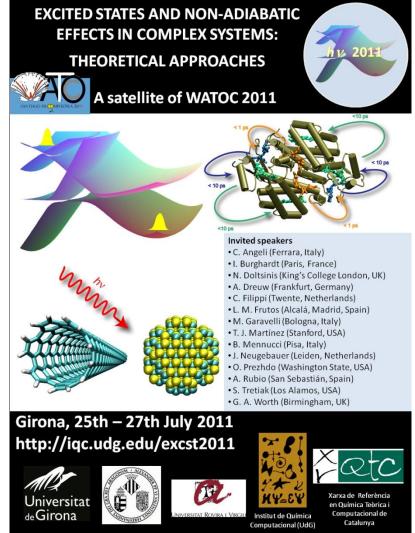


INVITATIONS

Excited states and non-adiabatic processes in complex systems. Theoretical approaches Girona (Spain), 25th - 27th July, 2011

The conference "Excited states and non-adiabatic processes in complex systems. Theoretical approaches" aims to provide a specialized forum on excited states and non-adiabatic processes. These subjects will be considered in their broadest sense. including methodological developments and their applications from molecular to large systems. Specific topics include:

- Conical intersections
- Excited state potential energy surfaces and dynamics
- Methodological developments
- Surfaces and photocatalysis
- Charge and energy transfer
- Biological and large systems
- Spectroscopy



The meeting is planned for approximately 100 participants. There will be 15 invited and 18 contributed lectures of 40 and 20 minutes, respectively, and a poster session. The organizers are Lluís Blancafort (chairman, Univ. of Girona), Mar Reguero (Univ. of Tarragona, Spain), and Carles Curutchet (Univ. of Girona). The conference web site is:

http://iqc.udg.edu/excst2011/

Kind regards Lluís Blancafort for the Organizing Committee

OPEN POSITIONS

Post-doctoral position IPREM-PAU (TOTAL funding) Opened January 2011 (12 months) In-situ photochemical production of endoperoxides

To be held in: IPREM UMR CNRS 5254 Université de Pau et Pays de l'Adour Hélioparc, 2 rue du Président Angot 64053 Pau cedex 9

People in charge:

TOTAL Petrochemicals: Michel DUC (<u>michel.duc@total.com</u>) **IPREM:** Sylvie LACOMBE (sylvie.lacombe@univ-pau.fr, tel : (33) 559 407 579) Thierry PIGOT (<u>Thierry.pigot@univ-pau.fr</u>, tel: (33) 559 407 433)

Aim of the research: Replacement of commercial peroxides for the initiation of styrene polymerization, avoiding stock and transport of highly unstable and nauseous products.

How to do it: In-situ production in an aromatic solvent of endoperoxides obtained by singlet oxygen addition on aromatic molecules such as polyacenes, terpenes...

Work to be done: The production of singlet oxygen in solution will be photochemically activated. The process is called "photosensitization": a photosensitizer is usually an aromatic molecule which absorbs UV or visible light and transfers its energy to ground state oxygen

by Inter System Crossing (ISC) to yield singlet oxygen in its Δg state. Singlet oxygen readily adds to alkenes or to aromatic molecules yielding endoperoxides by Diels-Adler [2 + 4] cycloaddition, hydroperoxides by addition on alkene bearing an allylic hydrogen atom, and 1,1-dioxetanes by addition on activated double bonds.

The photo-oxidation reaction should be made in order to fulfil several industrial requirements.

Required profile: Candidates with a PhD should be able to perform organic/photochemical synthesis, with a good knowledge of usual analytical procedures for the analysis of reaction products. Special skills for photochemical reactor design, up-scaling methods and photosensitized processes would be appreciated.

Conditions: The position will start in January 2011 and the TOTAL-IPREM contract is already signed. The position is for 12 months at least. Salary will be served by UPPA and will vary between 2100 and 2700 \notin "brut" depending on the experience of the candidate. The candidate will be interviewed by TOTAL scientific staff and Human Resources Services before engaging by UPPA.

ADDITIONS & CORRECTIONS

Photochemistry in Spain by Julia Pérez-Prieto *EPA Newsletter*, 2010, 32-55

1)

Photochemistry in Spain Julia Pérez-Prieto Molecular Science Institute (ICMOL) University of Valencia

2)

University Rovira i Virgili (URV), Tarragona

Centre: Faculty of Chemistry, Quantum Chemistry Group, Photochemistry Section.

Research group: Dr. Mar Reguero (Head of the Group), Dr. Maria Angels Carvajal, Yannick Mercier (PhD student), Mireia Segado (PhD student); Pablo Jiménez (PhD student)

<u>Research interests:</u> Computational elucidation of photoreaction mechanisms and rationalization of photophysical properties. Studies on the influence of substituents and environment in photochemical and photophysical properties. Types of systems/phenomena studied: Intramolecular charge transfer; Photocromism; Photomagnetism of organometalic complexes; Systems of biological interest.

<u>Special techniques:</u> Theoretical determination of the topology of the potential energy surfaces to locate crucial points (minima, transition states, conical intersections, real crossing) and reaction paths. Identification of main species involved in photophysical and photochemical phenomena and elucidation of reaction mechanism. Computational methods used: Multireference ab-initio methods, mainly CASSCF/CASPT2.

Recent publications

1. I. Gomez, M. Reguero, M. Boggio-Pasqua, M. A. Robb, J. Am. Chem. Soc. 2005, 127, 7119.

2. I. Gomez, M. Reguero, M. A. Robb, J. Phys. Chem. A 2006, 110, 3986.

3. M. Merchán, R. González-Luque, T. Climent, L. Serrano-Andrés E. Rodríguez, M. Reguero, D. Peláez, D., J. Phys. Chem. B 2006, 110, 2671.

4. M. A. Carvajal, M. Reguero, C. de Graaf, Chem Commun. 2010, 46, 5737.

5. A. Bányász, S. Karpati, Y. Mercier, M. Reguero, T. Gustavsson, D. Markovitsi, R. Improta, J. Phys. Chem. B 2010, 114, 12708.

MEMBERSHIP APPLICATION FORM

EUROPEAN PHOTOCHEMISTRY ASSOCIATION 2011 MEMBERSHIP RENEWAL/APPLICATION FORMPlease 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)									
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. Signature of the member: