European Photochemistry Association

NEWSLETTER

No. 91, December 2016

General information about the European

Photochemistry Association

is available at:

www.photochemistry.eu

Newsletter Editor: Prof. Maurizio D'Auria

Dipartimento di Scienze
Università della Basilicata
85100 Potenza, ITALY

ISSN 1011-4246

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

CONTENTS

EPA EXECUTIVE COMMITTEE

President

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

Newsletter Editor

Prof. Maurizio D'Auria
Dipartimento di Scienze
Università della Basilicata
Viale dell'Ateneo Lucano 10
85100 Potenza
Italy
maurizio.dauria@unibas.it

Treasurer

Dr. Alexandre Fürstenberg
Department of Human Protein
Sciences
University of Geneva
1211 Genève 4, Switzerland
Tel: +41 22 379 54 73
Fax: +41 22 379 55 02
Alexandre.Fuerstenberg@unige.ch

Mr Andrew J Keating
HORIBA Scientific
2 Dalston Gardens
Stanmore
Middlesex, HA7 1BQ
UK
Tel: +44 (0)20 8204 8142
Fax: +44 (0)20 8204 6142
andrew.keating@horiba.com

Past President and PPS matters

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

New Information Technologies

Prof. Dr. Roberto Improta
Institute for Biostructures and Bioimaging
Naples
robimp@unina.it

EDITORIAL

President's Letter

Dear EPA members,

We are witnesses of an interesting time of breakthroughs in which the light plays a crucial role and of increasing social awareness of the relevance of light-induced processes in humankind lives. The exciting "International Year of Light in 2015", in which many events/activities were held/undertaken throughout the world, acted as an excellent communication propeller.

The Nobel Prize in Chemistry 2016, awarded jointly to Jean-Pierre Sauvage, Sir James Fraser Stoddardt and Bernard L. Feringa, rewards the Laureates's achievements in the design and synthesis of molecular machines. The functionality of many of the molecular machines is based in the use of light and for sure this will motivate more investigation in the Photo-chemistry, Photophysics, and Photobiology research field.

Concerning the 2016 Porter's Medal, unusually the Ceremony has taken place at the end of the year. The two Porter Medals awarded, one to Professor James Barber FRS of Imperial College London and one to Professor Fredrick Lewis of Northwestern University, were received by the winners at the 9th Asian Photochemistry Conference (APC2016) held at the Nanyang Technological University (NTU), Singapore from the 4th to 8th December, 2016. As the President of the EPA, I had the honor of introducing Prof James Barber, while Prof Malcolm Forbes, Past President of the Inter-American Photochemistry Association, introduced Prof Frederic Lewis. Both Laurates presented lectures. I am very grateful to the APC2016 organizers, especially to the chairman Prof Edwin Yeow, for their warm hospitality and excellent arrangements in hosting the Porter's Medal Ceremony. In APC2016, Masuhara Lectureship Award was also held; information about this Prize is included in this issue.

Finally, I wish to inform that as it has traditionally done in its biannual conferences, the ESP will host a joint ESP-EPA Symposia in its 2017 congress, which will be held in Pisa (Italy) from 4 to 8 September 2017 with a symposium entitled "Drug photosensitivity and carcinogenesis."

Julia Pérez-Prieto

PUBLICATIONS

The 2016 Nobel Prize in Chemistry: Molecular Machines under the spotlight, a lot of photochemistry in the game!

Sebastiano Campagna
Department of Chemical Sciences, University of Messina, Messina, Italy

On october 2016, the Royal Swedish Academy of Sciences has awarded Jean-Pierre Sauvage (University of Strasbourg, France), J. Fraser Stoddart (Northwestern University, Evanston, USA) and Ben L. Feringa (University of Groningen, The Netherlands) the Nobel Prize in Chemistry 2016, "for the design and synthesis of molecular machines". Beside to be a prize honored to chemistry research, in opposition to recent Nobel prizes in Chemistry that brought some controversies for belonging, in most part, to the biology or physics realms, the Nobel Prize awarded to molecular machines has many debts to photochemistry!

Actually, in many respects the field of molecular machines is strictly interlocked (this word is not chosen by chance) with photochemistry.

(i) First, the awardees have tight connections with photochemistry: Jean-Pierre Sauvage has been involved in solar energy conversion since the beginning of his career in the seventies, and contributed to develop the field of photophysics of coordination compounds, particularly – but not exclusively - Cu(I) polypyridine complexes. Ben Feringa took advantage of the excited-state properties of organic molecules for making most of his molecular machines work. Fraser Stoddart, an extraordinary and innovative synthetic chemist, used the light, mostly in collaboration with Vincenzo Balzani, as the input triggering the movements and/or the output for revealing them.

(ii) Indeed, and this is the second connection between molecular machines and photochemistry, a molecular machine inevitably includes both synthetic aspects and issues connected to the possibility of inducing movements. As reported in the official document disclosed by the Royal Swedish Academy of Sciences describing the grounds of the Nobel Prize in Chemistry 2016 [1], a molecular-level machine can be defined as *"an assembly of a distinct number of molecular components that are designed to perform machinelike movements (output) as a result of an appropriate external stimulation (input)"* [2]. This indicates that, like the machines of the macroscopic world, even the molecular machines require energy to work. On dealing with molecular species, the obvious choice as the suitable energy source is the light. Actually, most of the synthetic molecular-level machines reported in literature are *light-driven molecular machines*, although electrochemically-driven and proton-driven (particularly relevant in the biological, natural systems) molecular machines also represent a valid option. This is indeed a very important point: most of the time, talking of molecular machines needs photochemistry concepts.

(iii) Third, light, or better the interaction of light with matter, is very often the key to evaluate whether a machine is really functioning, by taking advantage of various spectroscopic-sensitive outputs, luminescence being the most common one.

So, points (i)-(iii), leaving aside other aspects, make clear that the molecular machine realm has many contacts with photochemistry: it could be considered that the design itself of molecular machines must include equal contributions from synthetic chemists and scientists capable of predicting what is needed to activate the machines at the molecular level as well as to envisage a method to demonstrate that a work is made.

Design and synthesis of molecular machines was a long travel: some roots are in the development of synthetic approaches to unconventional, interlocked molecules. In this area, Jean-Pierre Sauvage's pioneering work on catenanes and knots, started in the eighties, represents a wonderful and – particularly at the time the first results were published – absolutely amazing and spectacular example [3]. Sauvage showed that properly-designed catenanes (and knots) could be synthetically made in acceptable yield, so fertilizing the area of the synthesis of complicated, interlocked systems. Then the rotaxanes came soon, brilliantly introduced by Fraser Stoddart: rotaxanes were initially seen as a particular form of host-guest species made of a roughly linear molecular species (the *axle*) introduced in the cavity of a ring-shaped molecule (the ring, again). When different subunits are incorporated in the axle, various molecular *stations* can be explored by the ring, which is seen as a molecular *shuttle*, an idea that implies the possibility of making the ring move upon some input [5].

Whereas such sophisticated intertwined molecules were synthesized, another concept was simultaneously developed, that was equally seminal to the foundation of molecular machines: the new concept, developed by Vincenzo Balzani, was the concept of photochemical molecular devices, introduced in April 1987 at the NATO Advanced Research Workshop on Photoinduced Charge Separation and Energy Migration in Supramolecular Species [5]. Here, beside basic ideas that strongly contributed to the research field of solar energy conversion and artificial photosynthesis, photoinduced conformational changes – already investigated by several researchers at the time - were explored, extremized and presented by a different angle, highlighting that supramolecular species could be designed and organized to perform (light-induced) high-valued functions, in other words to act like molecular machines (although the word needed some more years to be used) [2]. The same concepts were then fully developed, in a more clear and defined manner, in a book published by Balzani and Scandola few years later [6].

The marriage of the ability of masterizing the synthesis of complicated, interlocked supramolecular species, and of the idea of designing multicomponent species in which the photo-activation of conformational changes could produce useful work was the essential cornerstone on which molecular machines were built. Actually, synthetic and photochemistry research teams interacted very strongly in the following years, to lead the field to a full maturation, and finally allowing Balzani to introduce the concept of molecular machines [7].

The two next decades testified a terrific development for molecular machines. In the late nineties Ben Feringa strongly contributed to the field by preparing multicomponent systems ingenuily designed to be capable of monodirectional rotation (the so-called molecular rotors [8]), and through the development of light-driven molecular motors, he ultimately synthesized a now-famous molecular car, which attracted a lot of interest to the field, also from outside the academics [9], hitting the fantasy of people with possible potential future applications. Several other quite astonishing results were obtained by several research groups: Devens Gust and coworkers, who made an outstanding, obviously photoinduced artificial analogous of ATP synthases [10], David Leigh's group, who made a spectacular "small molecule walking down a track" [11], and Russ Kelly, who contributed to develop unidirectional molecular motors [12], are just a few of the talented scientists who made the molecular machines realm a quite impressive and exciting research area. I beg pardon to the many other researchers that I am not citing here explicitly. Obviously, the three Nobel Prize winners continued to contribute top articles to the field: I remember the intellectual enthusiasm I felt when "Jean-Pierre Sauvage made the muscles [13]!"

In general, probably the field of molecular machines is one of the best example showing that in Science the development of a research field is due to the contribution of many researchers, and that scientific knowledge evolves and proceeds like a unique multi-minded organism, where the contribution of any single researcher is based on, and is foundation for, the progress of Science itself. Photochemistry has played, is playing, and is foreseen to play in the future, major roles in the molecular machine field, particularly in connection with the energy source powering the molecular subunits (and as a consequence, on the choice of the molecular components to be used, whose photochemical properties must be well-known and suited to the specific scope). I congratulate the well-deserved Nobel Prize awardees and take the occasion of wishing all the best to the field, with a rainbow of perspectives shining on the horizon, waiting for the next move!

References and Notes

1. The Royal Swedish Academy of Science, Scientific Background on the Nobel Prize in Chemistry 2016, 5 October 2016, https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2016/advanced-chemistryprize2016.pdf, p.1.

2. This sentence, assumed in the document by the Royal Swedish Academy of Science as the definition for molecular machines, is taken from: V. Balzani, A. Credi, F. Raymo, J. F. Stoddart, “Artificial molecular machines”, *Angew. Chem. Int. Ed.* **2000**, *39*, 3348-3391.

3 C. O. Dietrich-Buchecker, J. P. Sauvage, and J. M. Kern, “Templated synthesis of interlocked macrocyclic ligands: the catenands”, *J. Am. Chem. Soc.*, **1984**, *106*, 3043-3045.

4 P. L. Anelli, N. Spencer, J. F. Stoddart, "A molecular shuttle", *J. Am. Chem. Soc.* **1991**, *113*, 5131–5133.

5 V. Balzani, L. Moggi, F. Scandola, "Towards a supramolecular photochemistry: assembly of molecular components to obtain photochemical molecular devices", in *Supramolecular Photochemistry* (NATO ASI Series 214, Ed. V. Balzani), Reidel, Dordrecht, **1987**, p. 1-28.

6 V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, **1991**.

7 *R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, "A photochemically driven molecular machine", Angew. Chem. Int. Ed.,* ***1993****, 32, 1301-1303.*

8 N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, "Light-driven monodirectional molecular rotor", *Nature*, **1999**, *401*, 152-155.

9 T. Kudernac, N. Ruangsupapichat, M. Parschau, B. Macla, N. Katsonis, S. R. Harutyunyan, K.-H. Ernst, B. L. Feringa, "Electrically driven directional motion of a four-wheeled molecule on a metal surface", *Nature*, **2011**, *479*, 208-211.

10 *G. Steinberg-Yfrach, J.-L. Rigaud, E. N. Durantini, A. L. Moore, D. Gust, T. A. Moore, "Light-driven production of ATP catalysed by* F_0F_1*-ATP synthase in an artificial photosynthetic membrane", Nature,* ***1998****, 392, 479-482.*

11 M. von Delius, E. M Geertsema, D. A Leigh, "A synthetic small molecule that walks down a track", *Nature Chem.*, **2010**, *2*, 96-101.

12 *T. R. Kelly, H. De Silva, R. A. Silva, "Unidirectional rotary motion in a molecular system", Nature,* ***1999****, 401****,*** *150–152.*

13 *M. C. Jimenez, C. O.* Dietrich-Buchecker, J. P. Sauvage, "Towards synthetic molecular muscles: contraction and stretching of a linear rotaxane dimer", *Angew. Chem. Int. Ed.*, **2000**, *39*, 3284–3287.

History of photochemistry and photophysics in France from the birth to the present

A guided tour of the laboratories across the "Régions"

Henri Bouas-Laurent, Jean-Pierre Desvergne
Institut de Chimie Moléculaire (Groupe Nanostructures Organiques), Université de Bordeaux, 33405 Talence
<h.bouaslaurent@cegetel.net>; <jpdesvergne@yahoo.fr>

Part II

Summary

In this account, we summarize the accomplishments of permanent researchers, whatever their nationality, in French laboratories from the beginning of the discipline. The emphasis is on the contribution of the main actors who followed one another in the research centres. Their involvement in various associations, organization of meetings, book writing, etc. are listed in several Tables (A-F). The text is not divided in topics but in research laboratories, which highlights the scientific and geographic environment of French research workers.

There is no distinct report on industrial chemistry as companies rarely unveil their results, but cooperation with industry is mentioned where appropriate. It should be noted that an important chapter devoted to industrial preparative photochemistry was published in the 1994 special issue of "L'Actualité Chimique".

In Part I after a general presentation, we surveyed the beginning of “Tour de France” by Ile-de-France and Bretagne-Pays de la Loire. The other Regions follow.

Aquitaine

Bordeaux (Université)

Chemistry

Laboratoire de Photophysique et Photochimie (Institut des Sciences Moléculaires from 2007)

As mentioned above, the laboratory was founded by *Joussot-Dubien* after his postdoctoral studies in New-York (1959). It developed rapidly to include *ca* 80 persons in 1984. The research activities of *Joussot-Dubien* were reported in several articles (Bouas-Laurent, EPA NL, 1998, 2009; L'Actualité Chimique 2009).
Previous work on photochemistry had been accomplished in the laboratory of organic chemistry by *Raymond Calas and Robert Lalande* (Calas and Lalande, 1959) on the photodimerization of anthracene derivatives. This research was pursued by *Henri Bouas-Laurent* (thesis in 1964, supervised by *Calas*) and his thesis students (1957-1974)(*vide infra*).

The first student of *Joussot-Dubien*, *Jean Faure* (*vide* Cachan and Mulhouse) investigated the fading mechanism of thiazinic derivatives in aqueous solutions using in parallel classical and flash spectroscopic methods. In 1964, *Jean Faure* and *Roland Bonneau* built a *microsecond* flash photolysis set up to observe and characterize the first intermediates of the dyes photoreduction.

Then, *Robert Lesclaux* (thesis with *Joussot-Dubien* 1968) worked on diverse chromophores in transparent solid matrices, such as boric acid. By measuring paramagnetism, he demonstrated, for the first time, that the phosphorescent state of fluorescein (whose lifetime is much longer in this matrix) is a triplet state (this had been only postulated before) (Lesclaux and Joussot-Dubien, 1964). He also showed the polycyclic aromatic hydrocarbons two photon excitation in boric acid glasses, leading to their *photoionisation at room temperature* (Joussot-Dubien and Lesclaux, 1964; Lesclaux and Joussot-Dubien, 1966).
In 1968, *Jean Faure, Roland Bonneau and Jacques Joussot-Dubien*, advised by *Lars Lindqvist* (*vide* Orsay) and Claude Barthelemy, engineer at the "Compagnie Générale d'Electricité (CGE), set up the first nanosecond flash photolysis apparatus emitting at 264.5 nm and

could observe the singlet-singlet excited state (S_1-S_n) transition of naphthalene in solution (Bonneau *et al.*, 1968; Bonneau *et al.*, 1969). These pioneering results were followed by similar work on benzene and mesitylene with *René Bensasson* (*vide* Orsay and Paris MNHN). *Bonneau*, after obtaining his thesis in 1971, was instrumental in discovering and characterizing the instable ground state of trans-1-phenyl-cyclohexene (in keeping with *Lionel Salem* and later with William Dauben)(Bonneau *et al.*, 1976). Moreover, as described further elsewere (Bouas-Laurent *et al.*, 2008), he characterized orthogonal triplet states (the elusive so-called phantom triplets) in the photochemistry of cyclenones (cyclohexenones, particularly with David Schuster- USA (Schuster *et al.*, 1984)) and arylethylenes (styrene, naphthylethylene and other arylethylenes synthesized by *René Lapouyade* (*vide infra*) in which a double bond has undergone a 90° twist on the path of a *cis-trans* isomerization. He also studied various mechanisms of photocyclization and of carbene formation from diazirines. *Bonneau* served as president of the "Groupe de Photochimie Français" de 1985 à 1993 (*vide supra*) and as a member of IUPAC where he contributed technical reports (Table F, a, b).

Joussot-Dubien oriented his research on solid matrices towards low temperature (77 K) electronic spectra discovered by Shpolskii, with *Michel Lamotte,* and then *Anne-Marie Merle* (a graduate from the Ecole of Chemical Engineering, Nancy) (Lamotte *et al.* 1974 and 1984). They were able to obtain and describe the Shpolskii spectra of diverse polynuclear aromatic hydrocarbons and their derivatives, *oriented in alkanes single crystals.* In 1989, *Lamotte* and *Joussot-Dubien* published, in cooperation with *Lina Nakhimovsky*, a detailed atlas that is considered to be an important reference (Table C, e). Attracted by the above research, *Marc Ewald*, moved from the *Bernard Muel* group at Orsay (*vide supra*) and joined the Bordeaux laboratory in 1972, to study the fluorescence of humic acids in fluvial and oceanic waters. *Philippe Garrigues* (a graduate from the Ecole de Chimie de Strasbourg, thesis in 1985 under the guidance of *Joussot-Dubien*), worked along these lines, observing a number of polycyclic aromatic hydrocarbons Shpolskii fluorescence (some of them synthesized by *Lapouyade*) and rapidly applied the technique to the detection and identification of oil in seas and oceans. He became an international expert in this domain and extended his expertise to analytical chemistry at large. He founded, in 1997, the "Laboratoire de Physico Toxicochimie des Systèmes Naturels (LPTC)"and, in 2007, became director of the

"Institut des Sciences Moléculaires" (ISM) that encompasses the activity of all the Bordeaux photochemistry.

Robert Lesclaux, following postdoctoral studies at the National Bureau of Standards (USA), left the solid state to explore the gaseous phase, focusing on the reactivity of free radicals (NH_2, peroxides, aromatic) useful to atmospheric and tropospheric modelisation (with *Françoise Caralp, Bernard Veyret, and Eric Villenave*) (Caralp *et al.*, 1999; Raoult *et al.*, 2004). Taking advantage of their neighbours' (*Jean-Claude and Marie-Thérèse Rayez*) expertise in theoretical chemistry, *Lesclaux and Veyret* (thesis Bordeaux 1983) determined the mechanism of the formaldehyde photooxidation (Veyret *et al.*, 1989). *Lesclaux* gave a lecture entitled "Kinetic studies of formaldehyde photooxidation" at the 11th International Conference on Photochemistry (ICP), College Park (Maryland, USA) in 1982. Later, in 1993, at the 16th ICP, at Vancouver (Canada), he was invited to describe his work on "The importance of peroxy radicals in the atmospheric oxidation of biogenic organic compounds". *Lesclaux* contributed a chapter in "L'Actualité Chimique", in 1994, on the photochemical reactions in natural media (Table B, a pp 64-69). He founded in 1980 the Groupe Français de Cinétique et Photochimie (GFCP) (Table A, d) and was instrumental in raising French gas phase photochemistry to an international level. In 1985, *Lesclaux* succeeded *Joussot-Dubien* as head of the laboratory until 1997 and then created a new larger body: the CRCM (Centre de Recherche en Chimie Moléculaire) that he led prior to its transformation into ISM (Institut des Sciences Moléculaires) in 2007 (*vide supra*, *Garrigues*). This change into larger research units was initiated by the CNRS, for the sake of administrative simplification.

Before leaving the direction of the laboratory, *Joussot-Dubien*, to provide new vistas to laser chemistry, set up a group, with *Gérard Dorthe, Michel Costes* and *Christian Naulin* aimed at study molecular dynamics of atomic or diatomic species in crossed beams at very low temperatures as those taking place in interstellar media (Dorthe *et al.*, 1985). Recent results of this team revealing the quantum behaviour of inelastic collisions between CO molecules and helium atoms were published in Science (Cheldeville *et al.*, 2013) and Nature Chemistry (Bergeat *et al.*, 2015). *Rayez* was fully associated for the theoretical aspect. The team now called "COMEX (Collisions Moléculaires en Milieux Extrêmes) is led by *Jean-Christophe Loison* and includes *Christian Naulin, Astrid Bergeat, Kevin Hickson.*

Sylvain Lazare started research in organic chemistry in Paris and after postdoctoral studies with Paul de Mayo (London, Canada) and Rangaswamy Srinivasan (IBM, Yorktown Heights, USA) joined the Bordeaux laboratory to investigate mechanisms using flash photolysis, prior to forming his own group devoted to laser ablation of polymers and biological tissues (Lazare and Granier, 1989). He is the author of an article on photoablation in "L'Actualité Chimique" in 1994 (Table B, a pp 116-119) and coauthor of a book in 1992 (Table C, g).

In 1974, the organic photochemistry group of *Bouas-Laurent* and his coworkers (*René Lapouyade, Alain Castellan and Jean-Pierre Desvergne*) joined the "Laboratoire de Photophysique et Photochimie Moléculaire" that had just been associated to the CNRS and merged rapidly with the teams, developing spectroscopic and photophysical skills. They completed the study of polycyclic aromatic hydrocarbon photodimerization, emphasising the stereochemistry (Bouas-Laurent *et al.*, 1972) and the role of excimers (Bouas-laurent *et al.*, 2000 and 2001). *Desvergne* and *Bouas-Laurent* carried out the first photochemical synthesis of a crown ether (Desvergne and Bouas-laurent, 1978). The team, with *Frédéric Fages*, pioneered the field of supramolecular photochemistry. They demonstrated the direct influence of a complexed metal cation upon the photoreactivity (Bouas-Laurent *et al.*, 1986; Table B, a pp 193-194) and detected metal cations by fluorescence, and notably excimer fluorescence (Table B, a pp 183-189). Remarkably, *Desvergne* was one of the first to explain the "non topochemical photoreactivity" in organic single crystals (Desvergne *et al.*, 1974). *Bouas-Laurent* gave a plenary lecture at the "VIIIth IUPAC Symposium of Seefeld", in 1980, entitled "From anthracene photodimerization to jaw photochromic materials and photocrowns" (Bouas-Laurent *et al.*, 1980). He coedited, with Heinz Dürr a book on photochromism in 1990 that was reedited in 2003 (Table C, h; see also Bouas-Laurent and Dürr, 2001 and Table F, c). *Desvergne* gave a plenary lecture at the "XIVth IUPAC Symposium of Leuven" in 1992, entitled "Tunable photoresponsive supramolecular systems" (Desvergne *et al.*, 1992). Later, *Desvergne* unveiled an efficient energy transfer in original low molecular fluorescent gels and was a lecturer on that topic at the XXIst IUPAC Symposium in Kyoto in 2006 (Desvergne *et al.*, 2006). *René Lapouyade*, in addition to his many synthetic contributions to the studies of *Joussot-Dubien, Garrigues,* *Lamotte and Bonneau*, illustrated himself in the photocyclization of unsaturated systems (Fornier de Violet *et al.*, 1978) as well as the design and study of intramolecular charge transfer systems for the selective recognition of ions and molecules by fluorescence (Malaval *et al.*, 2001) (Table B, a pp183-192). *Lapouyade* has also prepared original magnetic commuted photochromic systems (Maus et al., 1999). *Alain Castellan*, after research on photodimerization, started with *Bouas-Laurent* studies on the photoyellowing of paper in coordination with the Grenoble Paper Centre (Castellan *et al.*, 1990; Table B, a pp 148-155) and, in 1994, built his own laboratory (with *Stéphane Grelier*). He extended his investigations to a variety of papers and woods and became an international expert in the photochemistry of lignocellulosic materials (Castellan and Grelier, 2016).

Nanostructures Organiques (NEO) is one of the teams representing photochemistry in the ISM. The team is led by *Dario Bassani* (arrived in 1997) and includes *Jean-Luc Pozzo* (arrived in 1994), *André Del Guerzo* (arrived in 2002) and *Nathan McClenaghan* (arrived in 2002), all issued from external laboratories. *Pozzo* came one year after his thesis (1993, under the supervision of *Guglielmetti*) from Marseilles. He pursues investigations in the field of photochromic substances and is active in the "Groupe De Recherche (GDR)" in this area (*vide supra*, Cachan). He designed new photochromic gels (Ahmed *et al.*, 2002) and recently sophisticated photochromic systems displaying eight commutable states of different colours (Szaloki *et al.*, 2014). Pozzo was coorganizer of the "International Symposium On Photochromism (ISOP 2004)" at Arcachon. *Bassani* (thesis with F. D. Lewis, Northwestern University, USA in 1993, post doctoral studies with Jakob Wirz (Basel) and *Jean-Marie Lehn* (Strasbourg)) started research in Bordeaux in 1997 to develop supramolecular photochemistry. One of his first eminent results was the photodimerization of cinnamates templated by hydrogen bonds (Bassani *et al.*, 2000). More recent work is directed towards photochemical nanosciences: organic optoelectronic devices (Huang *et al.*, 2005). *Bassani* is editor in chief of "Photochemical & Photobiological Sciences (PPS) (Table D, d). He was chairman of the XXVth IUPAC Symposium on Photochemistry in 2014, Bordeaux (Table E, c) and coorganizer of an EPA symposium (Table E o). *Nathan McClenaghan* (thesis in 2000 with Prasanna de Silva "AP" at Belfast Northern Ireland) joined the CNRS in 2003 and was

appointed "Directeur de recherche" in 2012. He very actively develops research in supramolecular photochemistry, such as reversible energy transfer in excited states (Leydet *et al.*, 2007) photoinduced molecular topology *v.g.* exchange rotaxane-catenane (Tron *et al.*, 2015a) or reversible formation of a rotaxane (Tron *et al.*, 2015b). *Del Guerzo* (thesis in 1998 with Andrée Kirsch-De Mesmaeker, Bruxelles) is involved in the design and synthesis of luminescent molecular gels and other multicomponent assemblies where efficient energy transfers are observed and producing intense white emission (Del Guerzo, 2013). An in-depth study of the mechanisms is obtained using AFM and confocal fluorescence microscopy (Giansante *et al.*, 2011).
Moving from Rennes (*vide supra*) well known as a non linear optic (NLO) specialist (Mongin *et al.*, 2002), *Mireille Blanchard-Desce* joined the ISM in 2011 and pursues work on two photon induced fluorescence and photodynamic therapy; she has recently synthesized new organic *nanoparticles* displaying very *high stability and brightness* (Genin *et al.*, 2014); they are biocompatible and non-toxic systems that are alternative to quantum dots for bioimaging (Blanchard-Desce, 2013).
Thierry Toupance carries out nanostructures of semiconducting metal oxides and hybrid perovskite nanoparticles directed to applications in optoelectronics and photocatalysis in porous materials (Uddin *et al.*, 2012).

LCPO (Laboratoire de Chimie des Polymères Organiques)

Georges Hadziioannou obtained a degree in chemistry at Thessaloniki (Greece) and a thesis in Strasbourg in 1980; after postdoctoral studies in the USA, he was offered an industrial tenure by IBM (San Jose, California) and, later, a full professorship at Groningen (The Netherlands). In 2001, he moved again to Strasbourg as head of the Ecole Européenne de Chimie des Polymères et Matériaux. In 2009, he moved to Bordeaux to take a "Chaire d'Excellence" co-sponsored by CNRS, Région Aquitaine and Arkema (a Chemical Company). Among his accomplishments, those regarding *photochemistry* are Organic PhotoVoltaic (OPV) systems and flexible Organic Light ElectroLuminescent (OLED) devices (Stalmach *et al.*, 2000). Recent results were obtained with *Cyril Brochon, Eric Cloutet, Guillaume Fleury and Karim Aissou*...(Renaud *et al.*, 2012).

ICMCB (Institut de Chimie de la Matière Condensée de Bordeaux)

Claude Fouassier developed materials doped with luminescent cations (lanthanides) for applications as luminophores (Jubera *et al.*, 2003), as described in an article of « L'Actualité Chimique » (Fouassier, 2002). *Gilles Le Flem*, in the same laboratory, devoted a part of his activities to the fabrication of luminescent glasses.
Jean-François Létard, following his thesis supervised by *Lapouyade* in 1994, was a member of Olivier Kahn's team and developed photomagnetism, particularly when based on metal d-d transitions in transition metals coordination complexes (Létard *et al.*, 1997). *Létard* founded, in 2009, the start-up "Olikrom" (Bordeaux-Technopole) to make "smart", *i.e.* thermochromic, photochromic, piezochromic pigments. In the same group, *Corine Mathonière* (in cooperation with *Rodolphe Clérac* from the "CRPP" Centre de Recherches Paul Pascal) recently published a system (cyanometalate Fe/Co) acting as a molecular photochemical-thermal switch (Zhang *et al.*, 2014). She has also been associated with *Michel Verdaguer* and *Valérie Marvaud* (*vide* Paris) (Bleuzen *et al.*, 2009).

IMS (Intégration du Matériau au Système)

Lionel Hirsch, Guillaume Wantz and others in the team build their own photovoltaic devices and other systems in cooperation with some Bordeaux chemists, as well as organic electroluminescent diodes (Thakur *et al.*, 2011).

Physics

Before the start of the photochemistry in 1950-1960, photophysics was represented by *Alfred Kastler* and *Auguste Rousset* at the old "Faculté des Sciences", situated cours Pasteur, in the centre of the town. After a thesis in Paris on the fluorescence of mercury vapour, *Kastler* was appointed full professor of "general physics" in 1938. He cooperated with *Rousset*, *inter alia*, on the fluorescence of polyatomic molecules. After *Kastler*'s move to ENS Paris in 1942, *Rousset* was elected to the chair. In 1945, he founded the Laboratory of Molecular Optics.

Optique Moléculaire

Prior to his appointment in Bordeaux, *Auguste Rousset* studied physics at the University of Montpellier. Jean Cabannes was the supervisor of his thesis, 1935, on the diffusion of light. His field was the determination of structure of molecules and their organization in liquids and crystals, using the Raman effect and the luminescence.
Rousset formed a team with *Robert Lochet*, *Elizabeth Lafitte*, *André Massoulier* and *François Valentin*. They studied the molecular diffusion of light in liquids and gases (Rayleigh and Raman effects) as well as the luminescence of polyatomic molecules (Cadas *et al.*, 1962). They built their own set ups, notably fluoro- and phosphoroscopes to record low temperature spectra, to characterize aggregates and determine excited triplet states lifetimes. The laboratory grew with the arrival of *Guy Nouchy* (1958), *Pierre Loustauneau*, *François Dupuy*, *Jean-Pierre Chabrat*, *Jacques Mégel*, *Ross Brown* (now in Pau), *Jacques Rouch*, *Guy Goumet, Claude Vaucamps* and *Claudine Cazeau-Dubroca* (Loustauneau *et al.*, 1963). Between 1960 and 1980 a cooperation with chemists established bridges (Desvergne *et al.*, 1972).
In 1970, for family reasons, *Rousset* took a research fellow position at the University of Pau. *Guy Nouchi* recruited *Philemon Kottis* as full professor in place of *Rousset*. *Nouchi* and *Kottis* led the laboratory together until 1990 (*vide infra*). *Kottis* was a searcher in *Daudel*'s laboratory CMOA (see Part I) in the team of Roland Lefebvre. He was a specialist of the application of quantum chemistry to the spectroscopy resulting from a collective excitation: molecular polaritons, excitons etc. He gave the *Rousset* group a strong impetus in theoretical physics (Dupuy *et al.*, 1978).
One of his students, *Michel Orrit*, obtained his thesis (1984) under his guidance, and completed postdoctoral studies as Humboldt fellow with Hans Kuhn and Dietmar Möbius in Göttingen (1985-1986). Interested by hole burning, he made a breakthrough in revealing, with Jacky Bernard, the fluorescence of a *single molecule* (pentacene) in 1990 (Orrit and Bernard, 1990; Gaiduk *et al.*, 1999). In 2001, he was appointed to a full professor position at the University of Leiden (The Netherlands).

Guy Nouchi and *Claude Vaucamps* brought their expertise to the new group established by *Dorthe* and *Joussot-Dubien* to investigate the molecular dynamics of atomic or diatomic species in crossed beams (Dorthe *et al.*, 1985) at very low temperature (state-to-state chemistry).

CPMOH (Centre de Physique Moléculaire Optique Hertzienne)

In 1990, "Optique Moléculaire" was reorganized into a larger laboratory CPMOH led by *André Ducasse* (1990-1997).

In addition to the scientists cited above, the laboratory was composed of new members, *André Ducasse*, *Jean-Pierre Aimé*, *Wilfrid Claeys*, *Jean-Pierre Delville*, *Eric Freysz*, *Claude Rullière*, *Gediminas Jonusauskas*, *Yves Servant*, *Jean-Marie Turlet*, *Brahim Lounis, Fabrice Vallée, Laurent Cognet...*

André Ducasse (thesis in 1978 in Bordeaux) founded a group on laser applications. In 1996, he launched the CELIA (Centre Laser Intense et Applications) to accompany the construction of the "Laser Mégajoule" (laser fusion facility 1.8 MJ) at Le Barp (CEA 30 km South to Bordeaux). He was appointed in 1999 general director of the "Institut d'Optique, graduate school" in Palaiseau until 2003. He also played a major role in the construction of the "Institut d'Optique d'Aquitaine" (IOA).

Claude Rullière built, with *Jonusauskas*, a picosecond (and then a femtosecond) laser spectrometer to apply ultra-fast photophysics to study photochemical mechanisms. A cooperation was established with *René Lapouyade* (Lapouyade *et al.*, 1992; Dumon *et al.,* 1994), *Jean-Pierre Desvergne* (Desvergne *et al.*, 2001) and now *Nathan McClenaghan* (Leydet *et al.*, 2007).

Rullière was later head of scientific research of CEA Le Barp (South to Bordeaux). In 2001, he edited a comprehensive, pedagogic, collective book on ultrashort laser pulses "Femtosecond laser pulses; principle and experiments", which was reedited in 2005 (Rullière, 2005).

Eric Freysz applied his expertise of lasers to the study of non linear phenomenons in solid materials in cooperation with chemists of ICMCB.

Claudie Cazeau-Dubroca described a special case of fluorescence of molecules already twisted in the ground state in protic solvents (Cazeau-Dubroca *et al.*, 1989).

Successive directors of CPMOH after *André Ducasse*:
Claude Rullière (1997-2003), *Fabrice Vallée* (2003-2006), *Jean-Marie Turlet* (2006-2007), *Eric Freysz* (207-2011).

LOMA (Laboratoire Ondes et Matière en Aquitaine)

In January 2011, CPMOH underwent a change to become LOMA. The photophysical activity was maintained. *Jean-Pierre Delville* was appointed director. His scientific activity concerns laser/matter interactions such as non linearity in liquid mixtures, laser optofluidics and microfluidics as well as laser induced modification of polymer optical properties.

IOA (Institut d'Optique d'Aquitaine)

The "Laboratoire de Photonique Numérique et Nanosciences » founded in 2011 is located in this Institute. *Brahim Lounis*, coming from CPMOH, is a specialist worldwide of unique nanoobjets. His activities in photophysics are connected with those of *Orrit.*

Pau (Université de Pau et des Pays de l'Adour)

Laboratoire de Chimie Structurale

Jean Deschamps (thesis in Bordeaux with M.-L. Josien) founded the laboratory in the 1960s, when the so-called "Collège Universitaire" (renamed Faculté in 1968 and University in 1970) had just been built. His main research field was theoretical chemistry. A part of the research was oriented towards photochemistry with a strong background in theory of excited states. The team was composed of *Elisabeth Poquet, Marc Chaillet, Alain Dargelos* with the cooperation of *Henri Cardy, Kathy Larrieu, Claude Pouchan and Daniel Liotard* (the latter was appointed professor at Bordeaux in 1989). In the 1970s, the following salient features of their studies emerged: a static and dynamic model for hydrogen abstraction by excited carbonyl groups; an in depth study of small molecules reactions (methanol fragmentation, alkenes hydration...). In addition, an original method to determine *saddle points* of potential energy hypersurface was devised using *ab initio* computation.

Elisabeth Poquet (thesis in 1963 with Adolphe Pacault, Bordeaux) took into account the presence of the Lacq oil industry (very active at that time), represented by Elf-Aquitaine and then Atochimie and later Arkema (photonitrosation, photooxidation, photosulfochloration, photosulfohydration...) (Table A,a pp 34-65) to undertake collaborative research. Very early, together with *Cardy, Chaillet and Dargelos*, she investigated, *inter alia,* the direct photooxidation of alkylsulphides and characterized experimentally and theoretically charge transfer in sulphur-oxygen systems (Cardy *et al.*, 1985). The theoretical work was extended to molecular systems such as pyrazolones (Cardy and Poquet, 1981). With Jean Ollivier (Elf-Aquitaine) and *Jacques Poulicard*, she has tackled the use of initiators and sensitizers for photosulfohydration. *Claude Pouchan* pursues the theoretical studies applied to the spectroscopy of chemical species, from small molecules to larger ones such as graphene.

Sylvie Lacombe, from 1994, focused the group activities on photooxidation. She developed gas solid interactions, in particular singlet oxygen formation at the interfaces (Lacombe *et al.*, 2009), photoactivable hybrid materials producing process (immobilized organic photosensitizers such as 9,10-dicyanoanthracene (Blanc *et al.*, 2010), implementation of photocatalytic reactions for air purification (Kartheuser *et al.*, 2012). *Lacombe*, with *Sylvie Blanc, Thierry Pigot, Christophe Canteau* and *Ross Brown* (the latter, previously a physicist in the Laboratoire d'Optique Moléculaire in Bordeaux, is more involved in molecular dynamics and quantum computations), cooperate with other French laboratories engaged in air, water and soil depollution: Clermont-Ferrand (*Claire Richard*), Toulouse (*Esther Oliveros*, *Marie-Thérèse Maurette*) and, more recently Bordeaux (*Rénal Backov*). Lacombe and her team have filed several patents. In 2007, *Lacombe* was cocoordinator with *Tran-Thi*, of an important multiauthor article on photocatalysis used against pollutants in “L'Actualité Chimique” (Table B,b pp 79-93). She was the organizer of two European Conferences on Photocatalysis in Bordeaux (Table E,o). She is vice-president of the European Photocatalytic Federation and is in charge of establishing French and European standards for photocatalysis.

Laboratoire de Chimie Organique Physique

Geneviève Pfister-Guillouzo (thesis in Caen, 1963) first calculated electronic spectra of thioheterocycles, in cooperation with *Jean*

Deschamps and *Danièle Gonbeau*. Later, she oriented her research to photoelectron spectroscopy coupled with *ab initio* calculation. *Gonbeau* has pursued this research, *inter alia*, on luminescent solids in cooperation with several external laboratories, especially the ICMCB (Bordeaux).

Midi-Pyrénées

Toulouse (Université Paul Sabatier)

IMRCP (Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique)

Armand Lattes, after his thesis supervised by Georges Mignonac (1960) developed research in photochemistry in parallel to those in the ground state chemistry with a team composed of *Monique Rivière, Jean-Claude Micheau, Nicole Paillous, Esther Oliveros, Marie-Thérèse Maurette, Isabelle Rico…*

Together with *Rivière and Oliveros*, he discovered the photochemical rearrangement of oxaziridines that was called photo-Beckmann (Lattes *et al*., 1982). This reaction displays the inverse stereoselectivity to that known for the chemical Beckmann. This result was completed by a theoretical study conducted by *Oliveros* in cooperation with *Jean-Paul Malrieu* (*vide infra*). His group was also involved in the selectivity of photodimerization and photoisomerization in organized media (Rico *et al*., 1978).

Nicole Paillous (thesis with *Rigaudy*, Paris) joined the Toulouse laboratory in the 1970s. She cooperated with *Lattes* and *Micheau* on the stereochemical and kinetic aspects of the photoreduction of cyclic ketones prior to orienting herself towards photodermatology, photoimmunology and photomedicine (Gicquel *et al*., 2000); she studied in particular the photolysis of drugs in close collaboration with the Pierre Fabre Laboratory and the Toulouse veterinary school as well as the photochemical reactivity of ruthenium complexes with DNA with *Patricia Vicendon* (Gélis *et al*., 2003). In 2007, *Vicendon* coordinated an article in "L'Actualité Chimique" on aminoacids and proteins photochemistry (Table B,b pp 15-18).

Esther Oliveros (thesis with *Lattes* in 1977) was a coauthor (with André Braun and *Marie-Thérèse Maurette*) of "Technologie Photochimique" a book that filled a need in the photochemical community; it became a bestseller in the French version (1986) or the English translation (1991) (Table C,i) She then devoted her research activities to photobiology and environment (she was a member of the editorial board of "Journal of Photochemistry and Photobiology B" from 1993 to 2001 (Table D,c). She has applied photooxidation to air and water treatment, a field in which she is well-known, particularly for singlet oxygen chemistry (Legrini *et al.*, 1993; Pignatello *et al.*, 2006). *Oliveros* was coordinator (with *Marie-Laure Viriot*, *vide* Nancy) of the chapter "Photochimie Préparative Industrielle" in a special issue of "L'Actualité Chimique" (Table B,a pp 34-63). A part of her research activity took place in Switzerland and Germany. In addition to her collaboration with French laboratories (Clermont-Ferrand, Pau, Lyon) she maintained an active cooperation with South America.

Marie-Thérèse Maurette contributed to the book "Technologie Photochimique" (Table C, i) and conducted in depth investigations on environment protection by photochemical methods, as reviewed in a special issue of the "L'Actualité Chimique" in 2007 (Table B, b pp 61-79), for instance by using V-UV excimer lamps (154-253 nm) for the destruction of pollutants and pathogenic agents (Monneyron *et al.*, 2003). An alternative to TiO_2 based catalysators consists of fixing organic sensitizers on polymers or silica gels to generate singlet oxygen that acts against pollutants (for instance sulphides, in collaboration *with Sylvie Lacombe* (Cantau *et al.*, 2006).

Jean-Claude Micheau, after his thesis with *Lattes* in 1977 (*vide supra*) and postdoctoral studies with Ilya Progogine in Brussels, turned his attention to the thermodynamic and kinetic aspects of photochemistry. He developed an elegant kinetic analysis for photochromic systems; the method is detailed in the book of Crano and *Guglielmetti* (Table C,n vol 2, chap.3) and summarized in a technical report on organic photochromism (Bouas-Laurent and Dürr, 2001). This analysis also applies to time resolved NMR spectra, obtained by *Gaston Vermeersch* at Lille (Delbaere *et al.*, 2002). *Micheau* was coauthor with *Nakatani* (Cachan) of an article on photocommutation in 2008 (Table A,e pp 31-37). He was chairman in 2015 of a colloquium on photochromism in Corsica (*vide* Cachan).

Suzanne Fery-Forgues (thesis in 1986 with *Paillous*, postdoctoral studies at the Royal Institution, London) made a contribution to the detection of metallic cations by fluorimetry and electrochemistry using ferrocenyl compounds (considered at the time non fluorescent) and has more recently applied fluorimetry to laser-induced selective detection of aminoacids in blood (Fery-Forgue, 2013). She also devised fluorescent micro- and nanocrystals to be used as photosensitive sensors in collaboration with *Pansu* (Cachan) and *Galaup* (Orsay). *Fery-Forgues* coauthored an article entitled "Micro-et nanocristaux luminescents" in « L'Actualité Chimique » in 2008 (Table B,e pp 42-46).

Laboratoire de Physique Quantique

Jean-Paul Malrieu was a distinguished theoretical chemist specialized in the study of ground and excited states in the Daudel laboratory (CMOA) in Paris (Huron *et al.*, 1973) and a member of the "International Academy of Quantum Molecular Science" (Daudel, 1967) when he moved to Toulouse. He contributed to the theoretical study of the Photo-Beckmann reaction (*vide* above) with *Oliveros* (Oliveros *et al.*, 1979) and investigated the photoisomerization of organic conjugated systems. He was invited to give a plenary lecture at the Xth IUPAC Symposium at Interlaken (Swizerland), in 1984 entitled "Neutral versus Ionic Excited States of Conjugated Systems; Their Role in Photoisomerization" (Malrieu *et al.*, 1984). This work should be compared to that of Salem (*vide* Orsay).

Laboratoire de Chimie de Coordination

Azzedine Bousseksou and his team (especially *Lionel Salmon*) is well known for his accomplishments in photomagnetism for designing robust inorganic Fe(II) dinuclear complexes capable of permutation at the nanosecond scale (Bousseksou *et al.*, 2004). Some of the patents taken out by the team found commercial applications. This work is in line with those of Bordeaux (*Létard, Mathonière, Clérac*) and Paris (*Marvaud, Verdaguer*).

Isabelle Dixon (thesis in Strasbourg with *Sauvage*) is facing an important challenge consisting of replacing Ru(II) by Fe(II) (more abundant and less expensive) in coordination complexes in view of photophysical applications.

Languedoc-Roussillon

Montpellier

ENSCM (Ecole Nationale Supérieure de Chimie de Montpellier)

Magdeleine Mousseron-Canet and *Jean-Claude Mani* (1960-1980) were among the first, in France, to explore diverse aspects of molecular photochemistry, for instance ethylenic photoisomerization, benzene photooxidation or enzyme-coenzyme interactions using fluorescence. They published a textbook in French in 1969 (Table C,a). *Mousseron-Canet* gave a plenary lecture at the first IUPAC Symposium on (organic) Photochemistry in 1964, Strasbourg, entitled "Isomérisation Photochimique de Quelques Systèmes Polyéniques" (Mousseron, 1964).
David Lerner showed a strong interest in photobiology, notably the difficult problem of the photochemistry of vitamin A and the determination of the quantum yield. In 1977, he explored the photolysis of water in monolayers and micelles (collaboration with *Giannotti*, Gif-sur-Yvette) (Lerner *et al.*, 1982) and later photochemistry in natural and artificial membranes.

Institut Européen des Membranes

Patrick Seta was deeply involved in the study of photoinduced electron transfer in intramolecular charge transfer systems in membranes (Seta *et al.*, 1985).

Institut Charles Gerhardt

Jean-Olivier Durand (with his team and a group of the Institut des Biomolécules Max Mousseron, Faculty of Pharmacy) is making photodynamic therapy systems to target cancer cells (especially prostate) and destroy them using biphotonic irradiation (Vaillant *et al.*, 2015).

Perpignan (Université)

After working with *Lerner* on vitamin A, *Pierre Viallet* studied exciplex fluorescence of polynuclear heterocyclic compounds (1973). In cooperation with *Michel Deumié* and *Pierre Jacquignon*, he built a device to analyze the fluorescence of diverse substances absorbed by an isolated living cell (1978). He then focused on biological compounds.

Provence-Côte d'Azur

Marseilles

Université Saint Jérôme

Laboratoire de Chimie organique

Jacques Metzger, head of the laboratory, gave in 1963 "organic photochromism" to *Robert Guglielmetti* as a topic for his thesis in response to a request by the DRME (Direction des Recherches et Moyens d'Essais, a division of the National Defense) aimed at replacing the classical argentic photographic process by a technique based on "photochromic molecules". In 1967, *Guglielmetti* obtained his thesis entitled "Synthèse et propriétés de spiropyranes benzothiazoliniques photochromiques". This was the starting point of a long venture at the Marseilles University, interrupted by an appointment at Brest (*vide supra*), where he extended research in the field (1971-1983), see below Marseille-Luminy.

Laboratoire de Chimie Moléculaire et Pétroléochimie (Institut des Sciences Moléculaires)

Michel Chanon was coeditor of a book in 1988 on photoinduced electron transfer (Table C,d) and single editor in 1997 of a book on photocatalysis (Table C,m). *Michel Julliard* was coorganizer of the Aix-en-Provence IUPAC Symposium in 1976 (Table E,a). They both studied the photophysics of redox exchanges of phthalocyanins in relation with their therapeutic activity (Decreau *et al.*, 1999). They also investigated the singlet oxygen sensitization on solid supports, in cooperation with *Lacombe* (*vide* Pau) applied to the degradation of alkyl substituted aromatic compounds.

Isabelle Couturier-Tamburelli and her team have investigated the photochemistry of cyanopolyynes in the vacuum UV, as an important phenomenon in interstellar chemistry (Table B,c pp XV-XIX).

Université Marseille-Luminy

Groupe de Chimie Organique et Physique

In 1983, *Guglielmetti* was elected to a professorship at the University of Marseille-Luminy and continued expanding his group and developing cooperation with the glass company "Essilor" to provide spirooxazines that showed a better fatigue resistance than spiropyranes. The gamut of the systems investigated (with *Gérard Giusti, Corinne Moustrou, Vladimir Lokshin…*) extended to the chromene family, in collaboration with the PPG Industry Company (Pittsburgh Plate Glass, USA). From 1988 on, *André Samat* reinforced the group, especially on the topic "variable optical transmission materials", that expanded its synthetic field and mechanistic investigations (Baillet *et al.*, 1993; Samat *et al.*, 2001) as well as its industrial (Sextant avionique, La Cellophane (RP), l'Oréal, Aussedat-Rey, Gemplus-Gemato) or academic (France, Italy, Germany, Portugal, Russia) cooperations. In France, tight links with *Kellman and Tfibel* (Orsay), *Jean Aubard* (Paris VII), *René Gautron* (Grenoble) should be noted, as well as the cooperative design of an analytical tool, the so-called "Degraphot" to automatically determine the fundamental properties of photochromic substances and especially their "fatigue" ability (Bouas-Laurent and Dürr, 2001). In 2002, when *Guglielmetti* retired, *ca* 30 theses had been defended and 25 patents granted. In 1993, a new meeting was launched by *Guglielmetti* (Table E, g) called "International Symposium on Photochromism" (ISOP) that met with immediate success, underlining the importance of photochromism in photosciences and the leadership of *Guglielmetti.* The latter authored several reviews, notably in "Photochimie 94", a special issue of "L'Actualité Chimique" (Table B,a pp 90-94). In 1999, he published a book in 2 volumes (Table C,n), in cooperation with John Crano (PPG) who commercialized the now well-known organic photochromic lenses "Transition". *Samat* took over *Guglielmetti* as head of the laboratory up to 2008, with the assistance of *Frédéric Fages* (*vide* Bordeaux). The laboratory, since 2008, is included in a large institute named "Centre

Interdiscplinaire de Nanosciences de Marseille (CINaM)" led by *Fages*.

Rhône-Alpes

Lyon

Ecole Centrale Lyon

Pierre Pichat devoted his research activities to photocatalysis, whether the fundamental aspects (Serpone *et al.*, 1995; Pichat *et al.*, 2010) or the potential applications for depollution of air and water (Pichat, 2003 and 2010). A particular mention should be made for self-cleaning materials (Pichat, 2013). *Jean-Marie Hermann* (Hermann *et al.*, 1986) and *Chantal Guillard* (Cermenati *et al.*, 1997) took part to some of these works. *Pichat* authored reviews on photocatalysis (Pichat, 2014) and was on the editing board of several journals (Table D,g). He was the coordinator of the article "Photochimie et Environnement" in "L'Actualité Chimique" in 1994 (Table B,a pp 64-82). Since several years, he has been one of the 3 co-presidents of the annual international Conference "Semiconductor Photocatalysis and Solar Energy Conversion".
Jean-Paul Chauvet (Bioingénierie et reconnaissance génétique) studies the photophysical processes in membranes models.

ENS Lyon (Ecole Normale Supérieure)

Chantal Andraud, head of the chemistry laboratory, develops an important activity in the photophysics of lanthanides (Picot *et al.*, 2008), in the two-photon luminescence and in non-linear optics (Grichine *et al.*, 2014). Among her collaborations, that with *Patrice Baldeck* (Grenoble) is noteworthy.
Elise Dumont, a theoretical chemist specialized in excited states, especially nucleotides photochemistry, has recently proposed (with *Antonio Monari*, Nancy) a mechanism for the sensitization of DNA by benzophenone (Dumont *et al.*, 2015).

Université Claude Bernard

Laboratoire de Chimie Organique

Gérard Descotes discovered the acetalic photoreactivity of sugars, which he extended to oxygenated heterocycles. He demonstrated that in the Norrish II reaction, where diradicals are formed, stereospecific dioxaspiranones are produced through a stereoelectronic effect (a priori unexpected) (Bernaconi *et al.*, 1983).
Olivier Piva (Thesis in 1988 with *Pete*, *vide* Reims), appointed professor in Lyon in 1998, uses photochemistry as key steps in multistep synthesis (photodeconjugation, photocycloaddition).

Laboratoire de Photochimie

Bernard Pouyet (with *Pierre Méallier*) devoted his research activity to the photodegradation of pesticides in water using semi-conductors (Percherancier *et al.*, 1995). An original aspect of his work was the photodecomposition of thymine dimers through mercury complexes (1981).

IRCEL (Institut de Recherche sur la Catalyse et l'Environnement de Lyon)

Jean-Marie Hermann contributes to the development of processes for photocatalytic degradation of pollutants together with *Chantal Guillard* (Houas *et al.*, 2001). The same team finalized a device for combatting bad smells, notably in refrigerators (Guillard *et al.*, 2005). They were coauthors of an article on photocatalysis in 2007 in “L'Actualité Chimique” (Table B,b pp79-93). The efficiency of semi-conductors supporting materials is limited by their poor use of incident light and the bad access of pollutants to the irradiated surface. To improve these factors, *Guillard* realized active optical fibers coated with a TiO_2 based sol-gel (Danion *et al.*, 2004). These materials were observed by *Didier Robert* (Metz) using electron microscopy (Table B,b 83).
Jean-Marc Chovelon studies the superficial area of soils, leaves, surface waters for a better knowledge of the photochemical mechanisms of pollutants degradation (Table B,b pp 71-75, Lin *et al.*, 2009).

Physicochimie des Matériaux Luminescents

Bernard Moine makes new lanthanides based luminophores designed to provide a better lighting and consume less energy (Table B,b pp101-103; Moine and Bizarri, 2006).

Institut Lumière Matière

Christophe Dujardin investigated optical properties of diverse lanthanides to be used as scintillators. He is associate editor of "Journal of Luminescence" (Table D,f).

INSA (Institut National des Sciences Appliquées)

Bernard Claudel studies the photophysical properties of lanthanide ions and the photocatalytic systems (materials engineering) to be applied to the oxidation of organic compounds for effluent purification (Bideau *et al.*, 1995).

Grenoble

CEA Grenoble (Commissariat à l'Energie Atomique)
Renamed "*Commissariat à l'énergie atomique et aux énergies alternatives*" since 2009.

Laboratoire d'Electrochimie Organique et Analytique

Georges Cauquis (thesis with *Rigaudy,* ESPCI), was well-known as an electrochemist. With *Gilbert Reverdy*, he combined this technique with photochemistry. In the 1960s, they characterized the formation modes of respectively the S_1 and T_1 states of anthronylidene (Cauquis and Reverdy, 1967). Then, with *Jean-Claude Moutet*, *Reverdy* was one of the first to investigate the photoreactivity of radical ions (Moutet and Reverdy, 1982).

INAC (Institut des Nanosciences et Cryogénie)

Jean Cadet (thesis with the radiobiologist Robert Téoule in the 1970s) together with his group (mainly *Thierry Douki* and *Jean-Luc Ravanat*, theses in 1992 with *Cadet*) focused his research on the action of γ rays and then UV A and B on biological tissues, especially DNA and nucleic bases, in connection with mutagenesis (Cadet *et al.*, 2005). His autority in photobiology is recognized, as editor-in-chief of the journal "Photochemistry and Photobiology" (Table D,a). Of note are his activities for the "Société Française de Photobiologie" (Table A,e) and the "European Society for Photobiology" (Table A,f).

Thierry Douki pursues research in DNA photochemistry, with emphasis on the characterization of photoproducts (photodimerization, photoisomerization) as well as their formation mechanisms (Douki *et al.*, 2015). He continues collaborations with *Cadet* and also other colleagues in Grenoble and other research centres (CEA, Saclay, for instance). He is associate editor of "Photochemistry and Photobiology" (Table D,a).

Laboratoire de Chimie et Biologie des Métaux

Marc Fontecave (now professor at Collège de France) together with *Vincent Artero*, since the 2000s, were interested in the electro- and photocatalysis of water and protons reduction into dihydrogen using biomimetic models of hydrogenases (Fihri *et al.*, 2008). Another group, composed of *Stephane Ménage and Olivier Hamelin* found a new process for photocatalytic oxidation of sulphides (Hamelin *et al.*, 2011) (*vide* Pau).

Université Joseph Fourier

Laboratoire de Photochimie

Pierre Jardon investigated the photophysical properties of heterocyclic compounds (with *Jane-Marie Bonnier*) (Bonnier and Jardon, 1972), then of biliverdine (with *René Gautron*) (Petrier *et al.*, 1982) as well as hypericine and its derivatives (Dumas *et al.*, 2004).

Laboratoire de Spectrométrie Physique

In the 1960-1970s, *Jean-Pierre Blanchi* and his coworkers studied the photoreduction of aromatic heterocyclic ketones, determining the (n-π)* energy and the electronic distribution of the excited triplet state.

Hans-Peter Trommsdorf became well-known as a spectroscopist, especially for hole burning using laser irradiation of crystals at low temperature, for instance porphyrin in octane (Vockler *et al.*, 1977). He was invited to give a plenary lecture entitled "Spectral Hole Burning" at the Prague IUPAC Symposium in 1994 (Trommsdorf *et al.*, 1995). He has notably studied the molecular dynamics of some fluorescent diarylethylenes (Irie's photochromic substances, now known worldwide) (Ern *et al.*, 2001).

Patrice Baldeck realizes micro and nanostructured metallic (silver, nickel, copper) objects, using two-photon absorption. He also synthesizes so-called "biphotonic" organic molecules for 3D imaging by fluorescence spectroscopy in biosciences (cooperation with *Nicoud*, Strasbourg, *Attias*, UPMC Paris, *Andraud*, ENS Lyon) (Picot *et al.*, 2008; Grichine *et al.*, 2014).

Département de Chimie Moléculaire

Alain Deronzier (thesis in 1977 with *Georges Cauquis*) combines electrochemistry and redox photochemistry, mainly towards artificial photosynthesis. He discovered one of the very first examples of organic reactions catalyzed by $Ru^{2+}(bpy)_3$ complex (Cano-Yala and Deronzier, 1984) or by charge transfer complexes (Deronzier, 1984). He also made numerous molecular photoelectrodes (Cosnier *et al.*, 1985) and, with *Frédérique Loiseau and Jérôme Chauvin,* assemblies displaying strong photoinduced charge transfer separations on solid surfaces (Liatard *et al.*, 2013). More recently, with *Marie-Noëlle Collomb*, he developed systems (dyade type) for hydrogen photoproduction in aqueous phase (Stoll *et al.*, 2014; *vide* also *Odobel*, Nantes and *Poizat*, Lille).

Jean Lhomme and his team, have used photoactive markers in the synthesis and study of oligonucleotides.

Institut Néel (Groupe Matériaux)

Géraldine Dantelle (thesis in 2006 at ENSCP, Paris, supervised by *Michel Mortier*) devises and studies the spectroscopic properties of transparent luminescent oxyfluorated vitroceramic nanoparticles, doped with lanthanides in view of improving white light LEDs.

Auvergne

Clermont-Ferrand

Université Blaise Pascal

Laboratoire de Photochimie Moléculaire et Macromoléculaire

Jacques Lemaire (thesis with *Michel Niclause* at Nancy) founded the laboratory in the early 1970s. With *René Arnaud, Jean-Luc Gardette and Jacques Lacoste*, he investigated molecular reaction mechanisms such as photoisomerization of azobenzene or azoic derivatives, as well as free radical chain photoisomerization. He also became rapidly interested in the study of phototransformation and photoprotection of a large variety of polymer materials in relation with industrial companies. In 1982, he was invited to give a plenary lecture entitled "Photocatalytic oxidation of polyamids" at the IUPAC Symposium of Pau (France) (Lemaire, 1982). The fame resulting from this activity allowed the creation in 1987 of the "Centre National d'Evaluation de Photoprotection (CNEP)" that was one of the first laboratories having a tight link between University and Industry in France; CNEP met an industrial need in this domain and was an immediate success.

Another topic, bio-oriented, was the study of the sensitising properties of furocoumarins with *René Arnaud* and *André Deflandre* in 1979. *Deflandre* later became a photochemist for the l'Oréal company and established a durable research cooperation with the Clermont laboratory.

Together with the preceding topics, *Lemaire*, with *Pierre Boule* and *Michèle Bolte* investigated photochemistry in aqueous phase to understand the mechanisms of the transformations of micropollutants in the environment. At that time, current models did not take light into account. This research has allowed the understanding of phototransformation of hundreds of molecules mainly under solar irradiation, in diluted aqueous solution, at the surface of soils or plants (Table B,b pp 71-75).

Gardette (thesis in 1983 supervised by *Lemaire*) with *Agnès Rivaton, Mohamed Baba, Bénédicte Mailhot* and *Sandrine Morlat-Thérias*, described the progress accomplished by their team in the field of the photodegradation of polymer materials (such as bisphenol polycarbonates, nanocomposites, etc.) submitted to light and oxygen, using, in addition to spectrometry, atomic force microscopy (AFM) and differential scanning calorimetry (DSC) (Table B,e pp 25-30).

Arnaud was the coordinator and coauthor in 1994 of the important chapter "Evolution Photochimique des Macromolécules Naturelles et Synthétiques" (Table B,a pp 132-181).

Michèle Bolte, Pierre Boule and *Claire Richard* (with *Mohamed Sarakha* and *Gilles Mailhot*) were experts in a number of domains: mechanistic elucidation of photodegradation of micropollutants such as Fe(III)-complexed nitroloacetic acid, photonitrosation and photonitration of phenolic compounds, photooxidation sensitized by humic substances or transition metal complexes, photolysis of halogenated aromatic compounds, photocatalysis on ZnO (Table B,a pp 69-82; Boule *et al.*, 1999; Khodja *et al.*, 2001). This activity, applied to pesticides, resulted in several patents and collaborations with the main agrochemical companies.

Claire Richard was deeply involved in singlet oxygen photosensitizers (Ronzani *et al.*, 2013), in cooperation with *Sylvie Blanc and Sylvie Lacombe* (Pau) and *Esther Oliveros* (Toulouse). *Agnès Rivaton* and *Jean-Luc Gardette* developed active layers and nanocomposites for organic photovoltaic cells, in collaboration with the CEA, the University of Grenoble and the laboratory of testing and attestation of photovoltaic modules at "Le Bourget-du-Lac" (Chambon *et al.*, 2008).

Laboratoire de Chimie des Substances Naturelles

Jean-Claude Gramain (thesis with Marcel Fétizon in 1967, Ecole Polytechnique) was a synthetic organic chemist with a strong interest in photochemistry (cooperation with *Gardette*). Noteworthy is his elegant use of the 6-electron (p or n) photocyclization as key step to simplify and shorten the synthesis of polycyclic alkaloids (Benchekroun-Mounir N. *et al.*, 1993; Bois *et al.*, 2004)).

Institut de Chimie de Clermont-Ferrand

Anne-Marie Delort, Gilles Mailhot and *Laurent Deguillaume* investigate the influence of a biological component (microorganisms) upon the oxidation mechanisms in the clouds situated at the Puy-de-Dôme summit, in competition with the known free radical pathways (Delort *et al.*, 2015).

Rachid Mahiou (with a team of 7 coauthors) made luminescent hybrid nanoparticles (Boyer *et al.,* 2012, European patent) for the early detection of prostatic tumoral cells, allowing their use in biphotonic imaging (Adumeau *et al.*, 2015). These works are in keeping with those of *Durand* (Montpellier).

Jacques Lacoste (present head of the CNEP, *vide supra Lemaire*) and *Sandrine Thérias* have published a review on the recent fundamental and applied research on the polymers photoageing in "L'Actualité Chimique" (Lacoste and Thérias, 2015).

Alsace

Strasbourg

Université Louis Pasteur (renamed université de Strasbourg since 2008)

Institut Le Bel

The Strasbourg University inherited the division into Institutes from the German organization. The Institute of Chemistry has attracted brilliant researchers such as Guy Ourisson, superviser of *Jean-Marie Lehn's* thesis (1963). *Lehn*'s research led to the definition of a new field known as "supramolecular chemistry" detailed in an authoritative, often cited book (Lehn, 1995). Lehn has a multidisciplinary approach on a number of areas in chemistry. The following concerns only photochemistry.

In 1976, he was one of the first, with *Jean-Pierre Sauvage* (*vide* also *Amouyal*, Orsay) to study the photolysis of water by irradiation of metal complexes with solar light (Lehn and Sauvage, 1977; Kirch *et al.*, 1979). Together with *Raymond Ziessel*, he pursued these investigations as well as the photoreduction of CO_2 (Lehn and Ziessel, 1990). In 1993, with *Sylvain Gilat* and *Stephen Kawai*, *Lehn* synthesized photoinduced optoelectronic switches, built from Irie's diarylethylene photochromic systems (Gilat *et al.*, 1993). Later, the synthesis of photochromic metallic (Re, Ru, W) complexes was designed for the storage and non-destructive reading of optical data (Fernandez-Acebes and Lehn, 1998). In cooperation, especially with *Claude Hélène* (*vide* MNHN, Paris), he realized the direct photocleavage of HIV-DNA by quinacrine derivatives (Teulade-Fichou *et al.*, 2001). *Lehn* gave a plenary lecture entitled "Towards adaptive chemistry. Aspects of photochemical processes" at the Bordeaux IUPAC Symposium in 2014.

Lehn founded the renowned "Institut de Science et d'Ingénierie Supramoléculaire (ISIS), inaugurated in 2002. His present research is conducted at ISIS.

Laboratoire de Chimie Organominérale

After his work on the artificial photolysis, *Jean-Pierre Sauvage* (thesis in 1971 with *Lehn*) founded his own laboratory in 1980. He interested himself with several aspects of photochemistry, of which two themes emerge: (i) charge separation related to photosynthesis models (transition metal complexes or multiporphyrins) (Sauvage *et al.*, 1994); (ii) molecular machines moved by a photochemical signal (Sauvage, 1998; Collin *et al.*, 2001). Among his coworkers, *Jean-Paul Collin, Christiane Dietrich-Buchecker* (Dietrich-Buchecker *et al.*, 2001)*, Jean-Claude Chambon, Jean-Marie Kern and Valérie Heitz* made noteworthy contributions in these areas. *Collin* is coauthor with *Bassani* of an article in "L'Actualité Chimique" on supramolecular photochemistry, describing examples of rotaxanes and catenanes displaying photo-induced original topological properties (Table B,e pp 46-50). These activities are continued at ISIS.

Laboratoire de Photochimie (Ecole Européenne des Hautes Etudes des Industries chimiques de Strasbourg)

Charles Tanielian (postdoctoral studies with Brian Stevens, USA), is a specialist of mechanisms involving dioxygen in photochemical reactions (Table B,a pp 168-181). He also addresses the dioxygen deactivation mechanisms and has determined a number of reaction kinetics involving singlet oxygen (Table B,b pp 26-34; Tanielian *et al.*, 1996; Tanielian *et al.*, 2000). In 1994, he was instrumental in making phenalenone (a sensitizer) a universal standard to determine the singlet oxygen quantum yield (Schmidt *et al.*, 1994). Tanielian also examined the kinetic aspects of photocatalysis with polyoxotungstates (Tanielian *et al.*, 2003).

Following his work on water photolysis and carbon dioxide photoreduction, *Raymond Ziessel* (thesis with *Lehn*) devoted his research to artificial photosynthesis and charge transfer systems for protein biomarking (Ulrich *et al.*, 2005). He also cooperated with *Nicolas Leclerc* towards research on new organic photovoltaic systems.

Laboratoire de Chimie Organique Synthétique

Michel Franck-Neumann investigated the reductive photodecomplexation of iron carbonyl complexes and carbene photogeneration (Franck-Neumann and Lohmann, 1977).

Laboratoire de Chimie Quantique

Alain Veillard obtained a thesis under the guidance of Bernard Pullman, Paris, a member of the International Academy of Molecular Quantum Science (Daudel, 1967). Then, he founded with *Marie-Madeleine Rohmer* the Strasbourg Quantum Chemistry Laboratory. He became one of the best specialists of organometallic photochemistry, a difficult field dealing with excited states of transition metals, together with his team members *Chantal Daniel* (Daniel *et al.*, 1984) and *Alain Dedieu* (thesis 1972 with *Veillard*). *Daniel and Jacquemin* (*vide* Nantes) were coauthors of an article in « L'Actualité Chimique » entitled "Molécules et lumière, une histoire d'électrons" (Jacquemin and Daniel, 2014).

IPCMS (Institut de Physique et Chimie des Matériaux)

Jean-François Nicoud set up a team famous for the synthesis and study of molecules designed for NLO (Non Linear Optics) (Zyss *et al.*, 1984). He developed a great activity in biphotonic imaging (in this area, *vide* also *Jullien* (Paris), *Garcia, Durand* (Montpellier), *Baldeck* (Grenoble), *Blanchard-Desce* (Rennes and Bordeaux) and others).

Jean-François Nierengarten (thesis with Sauvage in 1994) formed a team focused on the photochemistry of transition metal complexes. He addressed strong charge transfer systems such as dendrimers incorporating C_{60} to increase its solubility and triplet lifetime for applications in limiting optic transition materials (Figueira *et al.*, 2006) or light emitting devices (Armaroli *et al.*, 2006). Recently, *Nierengarten* oxidized graphene and covalently linked it to C_{60} for an efficient electron transfer in view of application to solar cells (Barrejon *et al.*, 2014).

Laboratoire des Matériaux, Surfaces et Procédés

Nicolas Keller and *Valérie Keller-Spitzer* contribute to the progress of photocatalysis (Table B, b pp 79-93) for degradation of pollutants in carrying out inactivation of gaseous biological agents with photoactivated semi-conductors (Keller *et al.*, 2004).
Jean-Yves Bigot (NLO group) studies the first steps of the photochemical reactions using a femtosecond laser (Table B, b pp 19-24), especially green fluorescence protein.

Institut d'Electronique des Solides et des Systèmes

Abdelatif Slaoui makes inorganic nanocrystals for applications to photovoltaics (Collins and Slaoui, 2007).

Laboratoire de Biophotonique et Pharmacologie

Andrey S. Klymchenko (with *Yves Mély*...) applies fluorescence techniques to study interactions between molecules for biomedical imaging *in vitro* and *in vivo* (Reisch *et al.*, 2014).

ISIS (Institut de Science et d'Ingénierie Supramoléculaire)

ISIS was founded by Jean-Marie Lehn in 2002.

Luisa de Cola (with her team) addresses the fluorescence of transition metal complexes as markers for biomedical imaging (Mauro *et al.*, 2014a; Mauro *et al.*, 2014b).
Paolo Samorí (with *Emmanuele Orgiu*) developed organic transistors, based on optical commutation, incorporating photochromic systems (diatylethylene type), in cooperation with colleagues from Berlin, Bruxelles, Stanford (Orgiu and Samorí, 2014; El Gemayel *et al.*, 2015).

Mulhouse

Laboratoire de Chimie Organique Industrielle

Jean Meybeck , in the 1960s, was director of the "Ecole Supérieure de Chimie de Mulhouse", linked to the textile industry. His laboratory, including *Jean-Pierre Fleury* and *Jacques Streith*, investigated the problem of the yellowing of natural macromolecules such as wool and silk. As early as 1968, he set out to extend these studies to synthetic fibers and, to that end, recrute *Jean Faure* as a specialist of flash photolysis using lasers as sources of light (*vide* Bordeaux). Since then, photochemistry received a strong impetus from *Faure*.

Laboratoire de Photochimie des Hétérocycles

Jacques Streith was involved in the chemistry and photochemistry of heterocyclic compounds. He notably discovered the photochemical contraction of pyridines *N*-oxides into pyrroles and the rearrangement of ylids and pyridium amidates (Streith and Sigwalt, 1966). He was invited in 1976 to give a plenary lecture entitled "The photochemistry of aromatic ylids; rearrangement and fragmentation pattern" at the VIth IUPAC Symposium of Aix-en-Provence (Streith, 1977).

Laboratoire de Photochimie Générale

Jean Faure, soon after his arrival in 1969 formed a group constituted of *Patrice Jacques, Jean Schultz, Daniel-Joseph Lougnot, Jean-Pierre Fouassier, Louise Stauffer and Jean-Octave Eymann*. Their first works concerned picosecond laser (rare in France at that time) photophysics of a variety of molecules such as carbonyl derivatives, halogens, isomerization of some cyanines, cyclopropane or benzoine derivatives in a polymeric matrix. In parallel, *Faure* addressed with success the mechanistic studies of polymer photodegradation (mainly hydrazoic compounds) and the photostabilization of vinylic and acrylic polymers, in link with industry. He was invited to give a plenary lecture entitled "Laser Spectroscopical Methods for the Study of Primary Processes during the Photodegradation" at the "IUPAC Symposium on Polymer Chemistry" organized in 1976 by Georges Smets (Faure, 1977). The group grew in 1975 with *Christian Decker, Edouard Pénigault* and *Annick Goursot* as well as *André Braun* (on leave from the Ciba-Geigy Company). Then, the laboratory included 22 persons. In 1979, *Jean Faure* was appointed director of the "Laboratoire de Photophysique Moléculaire" at Orsay (*vide* Orsay) and *Fouassier* suceeded *Faure* as head of the laboratory. The following period was marked by a still wider opening to the world of industrial companies (SNPE (Société des Poudres et Explosifs,), Peugeot...) and to semi-public Research Institutes (CNRS: Groupe d'Intérêt Scientifique Cellulose-Papier, CNET (Centre National d'Etudes des Télécommunications)...). *Fouassier* (with *Jean-Alain Bousquet, Roger Salvin, Bernadette Graff, Fabrice Morlet-Savary, Jacques Lalevée...)* made himself known in the reactivity of initiators and sensitisers. This was accompanied with the publication of two books coedited with Jan F. Rabek (Table C,f and C,k) and a book written by him in 1995 "Photoinitiation, photopolymerization, photocuring" (Table C,l). *Fouassier* was coordinator and coauthor of the article "Polymère et lumière" in “L'Actualité Chimique" in 2008 (Table B,e pp 16-30). This research is still flourishing (Xiao *et al.*, 2015).

Lougnot, who took the lead after *Fouassier*, focused his studies on dyes and techniques of laser development (Fouassier *et al.*, 1987; Saimov *et al.*, 2003). An article of “L'Actualité Chimique” in 2008 highlights the group investigations (Table B,e pp 18-22). *Pénigault* and *Goursot* are specialists of theoretical chemistry (metallic clusters) (Sandorfy *et al.*, 1986). *Decker* proved particularly competent in applied photochemistry in polymer media (Decker, 1996). Owing to the collaboration with the CNET (*vide supra*) *Christiane Carré* joined the group in 1985 to develop transient networks spectroscopy and holographic recording, taking advantage of the Mulhouse group expertise in polymer photochemistry (Ibrahim *et al.*, 2012) (*vide* Brest). *Patrice Jacques* was especially involved in the photoinduced electronic transfer (Jacques and Allonas, 1994).

Laboratoire de Photochimie et d’Ingéniérie Macromoléculaires

Xavier Allonas, having joined the laboratory in 1996, reorganized in 2010, as well as *Lisette Lavielle* and *Carole Ecoffet*, became head, after *Lougnot*, of an active research laboratory, structured in the way of a department, combining basic and applied research (more than 30 granted patents). A review on the design of organic dyes for the free radical polymer initiation was published in 2014 (Ley *et al.*, 2014).

Institut de Sciences des Matériaux de Mulhouse (IS2M)

Carole Ecoffet, Jacques Lalevée, Fabrice Morlet-Savary, Olivier Soppera, Lavinia Balan... develop specific research in polymer photochemistry of materials: nanophotochemistry, lithography... A recent review on polymer photoinitiation appeared in the Beilstein Journal of Organic Chemistry (Lalevée *et al.*, 2014).

Lorraine

Nancy

Université de Lorraine

Département de Chimie-Physique et ENSIC (Ecole Nationale Supérieure des Industries Chimiques)

Michel Niclause was head of the laboratory and expert in kinetics and chemical engineering when photochemistry started expanding in France. In the 1970s, with his coworkers *Jacques Lemaire* (*vide* Clermont-Ferrand), *Jean-Claude André, Michel Bouchy* and *Xavier Déglise*, he studied the photochemical initiation of aldehyde chain oxidation reactions (André *et al.*, 1971).
Jean-Claude André was involved in molecular physics such as the deactivation of vibrationally hot excited state in the gas phase (1975), the implementation of industrial photochemical reactions (1980), and the kinetics of intermolecular excimer and exciplex formation ((1994). *André* is also a *pioneer* of stereophotolithography (precursor of the 3D printer). He deposited a first patent in 1984 (André *et al.*, 1984), an international patent in 1990 (André *et al.*, 1990) and others followed (*ca* 25). This area expanded considerably to become almost commonplace; with the market currently valued at several billions of euros (Table B,a pp 105-110; Bertsch *et al.*, 1997a; Bertsch *et al.*, 1997b). From their experience in the industrial photochemistry schools in Nancy in 1988 and 1990, *Jean-Claude André* and *Bernard Vannes* edited a book entitled "Techniques d'Utilisation des Photons" in 1992 (Table C,j). In 1986, *André* was invited to give a plenary lecture entitled "New Developments in Photochemical Technology" at the "First International Symposium on Organic Chemistry in Technological Perspective", Jerusalem (André *et al.*, 1986).
Marie-Laure Viriot, after a thesis in Nancy with *Jacques Levisalles* (1970) and postdoctoral studies with Howard Zimmerman (Madison, USA)

joined the *André* group in 1975 (André *et al.*, 1986). She was the coordinator of the section "photochimie préparative industrielle" for the special issue of "L'Actualité Chimique" in 1994 (Table B,a pp 34-63). She then oriented her research activities towards other fields, together with *Céline Frochot.* They have notably examined the behaviour of macromolecules in solution using fluorescence to characterize the solid-liquid interface (Jung *et al.*, 2005). *Viriot and Frochot* have also developed functionalized photosensitizers for application to vascular dynamic phototherapy (Frochot *et al.*, 2007). *Viriot* was coordinator of a chapter in « L'Actualité Chimique » in 2007 on the topic "La lumière et le vivant" (Table B,b pp 6-39). In the same issue, *Frochot* supervised an article on *photodynamic therapy* (Table B,b pp 26-34), with *Muriel Barberi-Heyob* and *François Guillemin* as coauthors from the Alexis Vautrin Centre at Vandoeuvre-lès-Nancy on the topic "photobiologie et cancer" (the other coauthors being from Evry, Orsay, Lille, Limoges, Metz, Nantes, Rennes, Strasbourg). Dynamic phototherapy federates numerous multidisciplinary groups (Frochot *et al.*, 2007). *Viriot* published an authoritative article on this topic (Viriot *et al.*, 2008). In 2015, *Frochot* coordinated another article in "L'Actualité Chimique" (Frochot *et al.*, 2015). In addition, she is the organizer of the International Conference "Photodynamic Therapy and Photodiagnosis Update", to be held in Nancy, 24-28 October 2016 (*vide supra*: European Societey for Photobiology).

LERMAB (Laboratoire d'Etude et de Recherche sur le Matériau Bois)
(ex Laboratoire de Photochimie Appliquée et de Physicochimie des Polymères)

Xavier Déglise started research with *Niclause.* He then studied the transformation of natural and synthetic macromolecules under light irradiation. By an in depth investigation of wood with *André Merlin*, he became a well-known expert for wood external treatment (as *Castellan* was for paper in Bordeaux). Consequently, he had numerous industrial collaborations. Déglise and Merlin were coauthors of a review in "L'Actualité Chimique" in 1994 (Table B,a pp 156-167).

Champagne-Ardenne

Reims

Université de Reims Champagne-Ardenne

Laboratoire de Photochimie Organique, then laboratoire des Réactions Sélectives et Applications

Jean-Pierre Pete (thesis in 1966 with *Jacques Levisalles* at Nancy and postdoctoral studies with Paul de Mayo, London, Canada) founded the “laboratoire de photochimie organique” in Reims in 1969. It should be emphasized that his thesis supervisor was the local organizer of the first IUPAC Symposium of Organic Photochemistry in 1964 at Strasbourg (*vide supra*: "International Conferences"). At that time, synthetic organic photochemistry was in full expansion. *Pete* trained a large group of coworkers: *Janine Cossy* (who succeeded *Jean Rigaudy*, ESPCI, Paris), *Charles Portella, Jacques Muzart, Olivier Piva, Patrick Pale, Françoise Hénin* and others. The research mainly involved ketones (α-epoxyketones and enones) then the enantioselective photodeconjugation of α,β-unsaturated esters catalyzed by chiral α-aminoacids. This remarkable reaction was used for the enantioselective synthesis of natural products (Pete, 1996). *Pete* was invited to give a plenary lecture at the XIth IUPAC Symposium Lisbon, 1986, entitled "Enantioselective photodeconjugation of conjugated esters and lactones" (Pete *et al.*, 1986).

In parallel with *Muzart* and *Pale*, he observed the formation of unsaturated carbonyl compounds by photolysis of η^3-allylpalladium complexes (Muzart and Pete, 1980). *Pete* made also himself known by his original contributions in the [2+2] photocycloaddition, used as key step in the synthesis of a number of natural products. *Cossy* (thesis in 1979 with *Pete*) completed the synthesis of bicyclic cyclopentanols by photoreducting cyclization of unsaturated ketones (Belotti *et al.*, 1985).

Charles Portella (thesis with *Pete*, 1978) examined the photochemical reactivity of sulphonic and carboxylic acid derivatives. An interesting result was the discovery of the photoreduction, in mild conditions, of carboxylic esters into alkanes in presence of HMPA-H_2O (HMPA is hexamethylphosphotriamide) (Deshayes *et al.*, 1975). This reaction was applied to the selective reductive defluoration of fluoroesters (Portella and Pete, 1985).

Norbert Hoffmann (thesis in 1992 with Hans-Dieter Scharf, Aachen), joined *Pete* for postdoctoral studies and was recruited in 1993 as a CNRS researcher in Reims. He continues successfully the development of photocycloadditions and photoinduced free radical reactions. He gave a plenary lecture entitled "Efficient Radical Addition of Tertiary Amines to Alkenes using Photochemical Electron Transfer" at the XXIth IUPAC Symposium of Kyoto, 2006 (Hoffmann *et al.*, 2006). In 2008, he contributed substantially to an article on Photochemical Organic Synthesis in "L' Actualité Chimique" (Table B,e pp 6-13). As recipient of the EPA and the journal "Photochemical & Photobiology Science" 2014 prize, he was invited to give a lecture at the XXVth IUPAC Symposium, Bordeaux, 2014, entitled "Photochemically induced radical reactions with furanone". His research develops now in photoredox catalysis, an area with important industrial ramifications.

Nord-Pas-de-Calais

Lille

Université

Laboratoire de Photochimie Organique Physique

Alain Lablache-Combier (thesis in 1964 with *Levisalles*) formed a team (*Serge Caplain, Azelio Castellano, Jean-Pierre Catteau, Axel Couture...*) oriented towards the mechanistic investigation of photochemical reactions of heterocyclic compounds: photosubstitution of 6-membered cycles, especially pyridine, photochemistry of quinoxaline in oxygenated solvents.

In 1973, he was the author of two reviews on the photoisomerization of aromatic compounds in "L'Actualité Chimique" (Lablache-Combier, 1973). In 1971, CIDNP (Chemically Induced Dynamic Nuclear Polarization) became a precious tool to investigate photochemical mechanisms. Thanks to the Kaptein rules (Kaptein, 1971) it was thus possible to determine the multiplicity (singlet, triplet) of an excited state from the NMR spectra. Using this method, *Lablache-Combier, with Gaston Vermersch, Jean Marko, Nadine Febvay-*

Garot and *Serge Caplain* conducted a number of studies, especially on the photoreactivity of anthracene and acridine derivatives with CCl_4 and heterocycles photochemistry. The authors have also assessed the cytotoxic power of some drugs and analyzed the nucleic acids photosensitization by phenothiazines (Marko *et al.*, 1983).

Lablache-Combier undertook a long cooperation with *Claude Loucheux*, a polymer chemist, investigating the photoreticulation of polysiloxanes and other polymers incorporating photoactive groups. *Lablache-Combier* was invited to give a plenary lecture entitled "Synthesis and properties of photoreactive polysiloxanes containing pendant functional groups" at the XIIIth IUPAC Symposium, Warwick, 1990 (Coqueret *et al.*, 1990).

Axel Couture (with *Pierre Claudon*) pursued the study of heterocyclic photochemistry with emphasis on the role of amines in the photocyclization of diphenylethylenes and photocyclization of enamides (Couture *et al.*, 1984).

Laboratoire de Chimie Moléculaire et Formulation

Jean-Marie Aubry (thesis with *Rigaudy*, ESPCI, Paris) joined the University of Lille in the 1980s. In Paris, he was already an expert in singlet oxygen chemistry. In particular, he had synthesized a water-soluble rubrene derivative to determine the sensitized photooxygenation kinetics in H_2O and D_2O; it could thus be demonstrated that the lifetime of singlet oxygen is 17 times larger in D_2O than in H_2O. He continued his research in Lille notably discovering that the mixture of a molybdate salt and H_2O_2 is an efficient and convenient source of singlet oxygen (Aubry, 1985). With *Véronique Nardello*, in 1996, he found a new transparent singlet oxygen sensor, allowing its titration in aqueous phase (Nardello *et al.*, 1996). Consequently, *Aubry* was able to successfully investigate the oxidative photodegradation of fragrance molecules (eugenol, lilial, β-citronellol...) and dyes used in perfumery (Ruyffelaere *et al.*, 2013).

Laboratoire de Physicochimie

Pierre Goumand, with *Pascal Devolder* and *Jean-Pierre Marteel* (as well as *Jean-Philippe Grivet*, Orléans) studied in 1971 the intermediate steps of the anthrone photolysis and, in 1973, the spectroscopic properties of the carbene anthronylidene (*vide Cauquis*, Grenoble). *Devolder* described, in 1979, the chemiluminescence of active nitrogen with pure or doped benzene polycrystals at 77 K.

Laboratoire de Chimie-Physique (Hautes Etudes Industrielles)

Gérard Lepoutre with *Marc De Backer, Pierre Jacquot, François-Xavier Sauvage, Antoine Demortier*
studied water photolysis induced by solar irradiation and sensitized by sulphonated zinc phthalocyanin complexes; they also investigated a photoelectrochemical process in presence of water-soluble dyes, in 1977. Using phthalocyanins as sensitizers, they could oxidize methylamine or reduce methylviologen (De Backer *et al.*, 1983).

LASIR (Laboratoire de Spectroscopie Infrarouge et Raman)

The development of the time resolved Raman spectroscopy in the 1970s was at the origin of a group formed by *Guy Buntinx, Olivier Poizat* and later joined by *Michel Sliwa*. This technique has the ability to provide *structural* characterization of short-lived transient species in the course of photochemical reactions. Examples of applications are the photochemistry of 4,4-bipyridine (De Waele *et al.*, 1999) and photochromic compounds (Sliwa *et al.*, 2010) or the bioluminescence of oxyluciferine and its synthetic derivatives (Ghose *et al.*, 2015), in collaboration with numerous groups specialized in the study of these systems.

Laboratoire de Physique (Faculté des Sciences Pharmaceutiques et Biologiques)

Gaston Vermeersch, Jean Marko and their team applied the techniques of ultra-fast NMR to the structural and kinetic studies of *photochromic systems*, such as a new series of quinolones in cooperation with *Micheau* (Toulouse) and *Samat* (Marseille) (Berthet *et al.*, 2006).

Conclusion

This survey of the photochemical activities in the French regions provides an assessment of the presence of the discipline. It emphasizes the accomplishment of a lot of researchers working locally with a strong opportunity of cross-fertilization between different fields, often in connection with the local environment. We apologize in advance for having omitted some individuals or groups, whatever our efforts to cover all laboratories' activities.

The birth of the French Group of Photochemistry in 1968 constituted a forum for national seminars frequently open to foreign visitors and a strong stimulus to develop the field. "L'Actualité Chimique" often favours the publication of important advances of French laboratories in the domain, as reflected in the text and Tables. The French community is now open worlwide as attested in the Tables listing the participation in international associations, conferences organizations, journals editing etc.

Most of the first articles were published in French journals (Comptes Rendus, Journal de Chimie Physique, Bulletin de la Société Chimique de France...). This practice restricted the readership and consequently the citation index. Rapidly, the situation changed and the papers were published in international journals in English, as can be observed in browsing through the references. The latter are a selection of the most representative and often cited papers in the area of photochemistry, photophysics, photobiology, spectrometry... They allow an overview of the French contributions to the progress of the discipline.

This overview suggests the following remarks, which are not confined to France:

§- there is a growing interaction between the classical disciplines: physical, organic, inorganic, biological chemistry. The main fundamental reactions seem to have been discovered; the main efforts apply to the determination of mechanisms and applications to analytical chemistry, materials sciences and life sciences.

§- the advancement of photochemistry was favoured by the lightning progress in laser techniques (milliseconds to femtoseconds), optical equipment (AFM, STM, confocal fluorescence microscopy...) rapid electronics, computer controlled spectrometry (UV, IR, NMR) and quantum calculation methods.

§- the present trends in research emerge in this account:

- biological sciences, such as bioimaging, photodynamic therapy...
- materials sciences: artificial photosynthesis, photovoltaics, nanomaterials, lighting, information storage, bright display...

- chemical sciences: key steps in synthesis, supramolecular photochemistry...
- Environmental chemistry: green chemistry; air, water soil depollution.

One observes also an increase in interlaboratory cooperation encouraged by national, European and other international projects.

Acknowledgements

The authors are particulary grateful to the following colleagues for the information on their activities and their research centres.

Xavier Allonas (Mulhouse), Jean-Claude André (Nancy), Guy Buntinx (Lille), Jacques Delaire (Cachan, Orsay), Alain Deronzier (Grenoble), Suzanne Fery-Forgues (Toulouse), Robert Guglielmetti (Marseille), Sylvie Lacombe (Pau), Robert Lesclaux (Bordeaux), Marie-Thérèse Maurette (Toulouse), Dimitra Markovisti (CEA, Saclay), Monique Martin (Paris), Fabrice Odobel (Nantes), Esther Oliveros (Toulouse), Jean-Pierre Pete (Reims), Pierre Pichat (Lyon), Claire Richard (Clermont-Ferrand), André Samat (Marseille), Jean-Pierre Sauvage (Strasbourg), Bernard Valeur (CNAM), Marie-Laure Viriot (Nancy).

We appreciate also the advice and encouragement of the following foreign colleagues.

Silvia Braslavsky (Mülheim), David Worrall (Loughborough, GB), Jakob Wirz (Bâle), Heinz Dürr (Sarrebruck), Fred Lewis (Evanston, EU), Dick Weiss (Washington).

Special thanks are due to Dario Bassani for his critical reading of the manuscript and linguistic assistance.

Table A

Photochemical Associations

a) The "Groupe de Photochimie Français" (1968), turned into "Groupe Français de Photochimie, Photophysique et Photosciences (GFP2P)" in 2008, (E. Amouyal, président). The 40th anniversary of the association was celebrated during a group meeting organized by Amouyal at Palaiseau in November 2008 ; cf. *EPA NL*, **2009**, *79*, 108-111.

List of the participants to the first meeting of "Groupe de Photochimie Français" (9 février 1968)

Theoreticians

- O. Chalvet (Paris)
- R. Daudel (Paris)
- C. R. Guerillot (Rennes)
- J. P. Malrieu (Paris)
- L. Salem (Orsay)

Organic chemists

- J.-J. Basselier (Paris)
- G. Beugelmans(Gif)
- H. Bouas-Laurent (Bordeaux)
- G. Cauquis (Grenoble)
- P. Courtot (Brest)
- A. Lablache-Combier (Lille)
- R. Lalande (Bordeaux)
-. J. Levisalles (Nancy)
- J. C. Mani (Montpellier)
- Mme E. Montaudon (Bordeaux)
- Mme M. Mousseron-Canet (Mpellier)
- M. Pfau (Paris)
- B. Pouyet (Lyon)
- J. Rigaudy (Paris)
- G. Rio (Paris)

Physicochemists

- Mme A. Bernas (Orsay)
- J. Bourdon (Paris)
- Mme Dran (Lille)
- G. Emschwiller (Paris)
- P. Goudmand (Lille)
- Mlle Ivanoff (Orsay)
- J. Joussot-Dubien (Bordeaux)
- S. Leach (Orsay)
- J. Lemaire (Nancy)
- L. Lindqvist (Orsay)
- M. Niclause(Nancy)
- M. Poquet (Pau)
- J. L. Seris (Pau)
- Mme C. Vermeil (Paris)

b) European Photochemistry Association (EPA). J. Joussot-Dubien (1976-1979), D. Markovitsi (2007-2010), presidents.

c) Club EDF. J. Millet (Direction des Etudes et Recherche EDF) constituted a club « Photochimie-Electrochimie » in order to support the interaction between researchers from industry and university. J. Joussot-Dubien was the first president; J. Faure with C. Bailleux as EDF officer overtook him. In 1989, the section « Photochimie » included 33 members. The club organized theme-centred meetings and supported the club members to attend international conferences. The club sponsored and edited the special issue « Photochimie 1994 » of "L'Actualité Chimique".

d) Groupe Français de Cinétique et Photochimie (GFCP). Founded in 1980 by R. Lesclaux in order to bring together once a year specialists of combustion, gas phase kinetics, photochemistry and theoretical chemistry. The first meetings took place in Paris (ESPCI) and then in diverse French towns.

e) Société Française de Photobiologie (SFPb), E. Sage president since 2008.

f) European Society for Photobiology, (ESP), E. Sage president, 2011-2013.

Table B

Special Issues and Accounts in "l'Actualité Chimique"

a) *L'Actualité Chimique*, **1994**, « Photochimie 94 », suppl. TO n° 7, 4-210 (*39 authors*).
b) *L'Actualité Chimique*, **2007**, « photochemistry for a better life», n°*308-309*, 5-119, T.-H. Tran-Thi and E. Amouyal, coordinators (*97 authors*). An article (UV and skin) from the "Pierre Fabre" research institute by A. Mavon and D. Bacqueville, pp 35-39, is noticeable.
c) *L'Actualité Chimique*, **2008**, account on the « interstellar molecules and space photochemistry », *315*, II-XXIV, coordinated by S. Leach and E. Amouyal (*20 authors*).
d) *L'Actualité Chimique*, **2008**, account on « radiation chemistry», n° *316*, II-XX, coordinated by J. Belloni (*4 authors*).
e) *L'Actualité Chimique*, **2008**, « Photochemistry to transform matter», *317*, 5-64, coordinated by E. Amouyal and T.-H. Tran-Thi (*47 authors*). The article by H. Strub (scientific director of Sartomer, a branch of "Total"), on an industrial aspect of polymerization should be pointed out.
f) *L'Actualité Chimique*, **2015**, « la Chimie Fête la Lumière », *397-398*, 11-107, coordinated by T. Gustavsson and J. Belloni (66 authors).

Table C

BOOKS AND COLLECTIVE VOLUMES

a) « *Photochimie et Réactions Moléculaires* », Mousseron-Canet M., Mani J.-C., Dunod, Paris, 1969.
b) « *Eléments de Photochimie Avancée* », Courtot P. editor), Hermann Paris, 1972.
c) « *Photophysics and Photochemistry above 6 eV* », Lahmani F. (ed.), Elsevier, Amsterdam, 1985.

d) « *Photoinduced Electron Transfer* », Fox M. A., Chanon M., (eds), part B, Elsevier, 1988.
e) « *Handbook of Low Temperature Electronic Spectra of Polycyclic Aromatic Hydrocarbons* », Nakhimovsky L., Lamotte M., Joussot-Dubien J., Elsevier, 1989.
f) « *Lasers in Polymer Science and Technology: Applications* », Fouassier J.-P., Rabek J.F. (eds), CRC press, Boca Raton, 1990.
g) « *Laser Ablation of Electronic Materials: basic mechanisms and applications*" Fougarassy E., Lazare S. (eds), North Holland Amsterdam, 1992.
h) « *Photochromism: Molecules and Systems*", Dürr H., Bouas-Laurent H. (eds), Elsevier, Amsterdam, 1st edition 1990, 2nd edition 2003 (**1690** citations).
i) « *Technologie Photochimique ; Aspects Fondamentaux et Applications Industrielles de la Photochimie Préparative »,* Braun A., Maurette M. T., Oliveros E., Presses Polytechniques Romandes, Lausanne, 1986 (**1200** volumes sold). "*Photochemical Technology*", J. Wiley Chichester, 1991 (**2500** volumes sold).
j) « *Techniques d'Utilisation des Photons. Principes et Applications* », André J.-C., Vannes A. B. (eds), DOPEE85 Electra, 1992.
k) « *Radiation Curing in Polymer Science and Technology* », Fouassier J.-P., Rabek J. F. (eds), Chapman and Hall, Elsevier, London, 1993.
l) « *Photoinitiation, Photopolymerization and Photocuring. Fundamentals and Applications*», Fouassier J.-P., Hanser Gardner Publisher, Münich, 1995.
m) « *Homogeneous Photocatalysis* », Chanon M. (ed.), J. Wiley and sons, New York, 1997.
n) « *Organic Photochromic and Thermochromic Compounds* », Crano J.C., Guglielmetti R. (eds), vol. 1 and vol. 2, Plenum, New York, 1999, reprinted in 2006.
o) « *New Trends in Fluorescence Spectroscopy. Application to Chemical and Life Sciences* », Valeur B., Brochon J. -C., (eds), Springer-Verlag, Berlin, 2001.
p) « *Molecular Fluorescence. Principles and Applications* », Valeur B., Berberan-Santos M. N., Wiley-VCH, Weinheim, 1st edition 2001, 2nd edition 2012.
q) « *Lumière et Luminescence* », Valeur B., Belin ("pour la science"), Paris, 2005.

r) « *Réactions Ultrarapides en Solution ; Approches Expérimentales et Théoriques* », Mostafavi M., Gustavsson T., CNRS éditions, Paris, 2007.
s) « *Energy Dissipation in Molecular Systems* », Tramer A., Jungen C., Lahmani F., Springer, Berlin, 1st edition 2005, 2nd edition, 2010.
t) « *La Couleur dans tous ses Eclats* », Valeur B., Belin, Paris, 2011 (prize: "Le goût des sciences" 2011, prize : "Prisme" 2012, prize: "Roberval" 2013).
u) « *La Lumière et la Vie* », Valeur B., Bardez E., Belin, Paris, 2015.
v) "*Photocatalysis and Water Purification: From Fundamentals to Recent Applications*", P. Pichat (Ed.), Wiley-VCH, Weinheim, 2013.

Table D

Journals Editorial Boards

a) Photochemistry & Photobiology (J. Wiley) Editor in chief: J. Cadet (CEA, Grenoble Associate Editor: T. Douki (CEA, Grenoble).
b) J. Photochem. Photobiol. (A) Chemistry. (Elsevier) Editor for Europe: M. M. Martin (Paris). editorial board: J. Delaire (Cachan) J.-P. Desvergne (Bordeaux), K. Nakatani (Cachan),B.Valeur(CNAM).
c) J. Photochem. Photobiol. (B) Biology. (Elsevier) editorial board : D. Averbeck (Orsay), R. V. Bensasson (Paris), E. Oliveros (Toulouse).
d) Photochem. Photobiol. Sci. (Royal Society of Chemistry). Editor-in-chief: D. Bassani (Bordeaux). editorial board: E. Sage (Paris), D. Markovitsi (CEA, Saclay), L. De Cola (Strasbourg). The journal now belongs to EPA, ESP, Asia & Oceania Society for Photobiology and the Korean Society for Photoscience.
e) J. Fluorescence (Plenum). Associate editor: B. Valeur (Paris) 1995-1998 et 2002-2010.
f) J. Luminescence (Elsevier). Associate editor: C. Dujardin (Lyon).

g) J . Adv. Oxid. Technol. (Sci. Technol. Network); J. Environ. Sci. Health A (Taylor & Francis); Int. J. Photoenergy (Hindawi); Molecules (MDPI). Editorial committees : P. Pichat (Lyon).

Table E

Organization of International Conferences in France

a) 6th IUPAC Symposium on Photochemistry, Aix-en-Provence, July 1976, president: K. Schaffner, co-organizers: J. Kossanyi and M. Julliard.
b) 9th IUPAC Symposium on Photochemistry, Pau, July 1982, president: J. Joussot-Dubien, co-organizers: H. Bouas-Laurent and E. Poquet.
c) 25th IUPAC Symposium on Photochemistry, Bordeaux July 2014, president: D. Bassani, co-organizers: A. Del Guerzo and N. McClenaghan.
d) 5th International Conference on Photochemistry (ICP), Bordeaux, 1971, president: A. Noyes, local organizer: J. Joussot-Dubien.
e) 15th International Conference on Photochemistry (ICP), Paris, 1991, organizer: J. Kossanyi.
f) 6th International Conference on Solar Energy Conversion and Storage, Paris 1986, president: J.-M. Lehn, organizer: J. Kossanyi.
g) 1st International Symposium on Photochromism (ISOP-93), Les Embiez, September 1993, founding president: R. Guglielmetti.
h) 4th International Symposium on Photochromism (ISOP-2004), Arcachon, September 2004, copresidents: J.-P. Desvergne and J.-L. Pozzo.
i) 6th International Conference on Methods and Applications of Fluorescence Spectroscopy (MAFS), Paris 12-15 Septembre 1999, copresidents: B. Valeur et J. C. Brochon.
j) 6th International Conference on Femtochemistry, Paris, 6-10 July 2003, co-presidents M. Martin et J. T. Hynes.
k) Franco-Japanese Colloquium on Photochemistry, Bordeaux, 1979, CNRS, DGRST, organizers J. Faure and J. Joussot-Dubien.

l) Joint Meeting of Italian-French Photochemistry Groups, La Baume-lès-Aix, 25-28 October 1989, coorganizers R. Bonneau et A. Albini.
m) 11th Congress of the European Society for Photobiology, Aix-les-Bains, 3-8 September 2005, president: E. Sage.
n) 2nd Franco-Italian Symposium on Photosciences (Fisphoton), Marseille-Luminy, 7-10 December 2009, organizers E. Amouyal et S. Campagna.
o) EPA Symposium « Photochemical and Photobiological Methods for Solar Energy Conversion » organized par D. Bassani as an additional colloqium to the « 13th European Conference for Photobiology », Wrocław, September 2009.
p) Joint meeting of Italian and French Societies for Photobiology, Paris, 25-26October 2010, organizer: E. Sage.
q) Journées Européennes de la Photocatalyse (JEP), Bordeaux, 2009 et 2011, president: S. Lacombe.

Table F

French Contributions to IUPAC Technical Reports

a) Bonneau R., Carmichael I., Hug G. L., *PAC*, **1991**, *63*, 289-299. « *Molar Absorption Coefficients of Transient Species in Solution* »
b) Bonneau R., Wirz J., Zuberbühler A. D., *PAC*, **1997**, *69*, 979-992. « *Methods for analysis of transients Absorbance Data* ». **N.B.** *Roland Bonneau* was IUPAC titular member : 1986-1998 and secretary of the Photochemistry Commission : 1994-1998.
c) Bouas-Laurent H., Dürr H., *PAC*, **2001**, *73*, 639-665 (**570** citations). « *Organic Photochromism* ». **N.B.** *Henri Bouas-Laurent* IUPAC associate (1996-1998) then titular member (1998-2004).
d) Ameloot M., van deVen M., Acuña A.U., Valeur B., *PAC*, **2013**, *85*, 589-608. « *Fluorescence Anisotropy Measurements in Solution: Methods and Reference Materials* ».
e) Lemmetyinen H., Tkatchenko N. V., Valeur B., Hotta J., Amelot M., Ernsting N. P., Gustavsson T., Boens N., *PAC*, **2014**, 86, 1969-1998. « *Time Resolved Fluorescence Methods* ». **N.B.** *Bernard Valeur* was a member of the Physical and Biophysical Chemistry Division (2004-2010).

References

Adumeau P., Leccia F., Boyer D., Canet J.-L., Gautier A., Morel L., Gefflaut T., Mahiou R., *L'Act. Chim.*, **2015**, *395*, 23-28.

Ahmed S. A., Sallenave X., Fages F., Mieden-Gundert G., Müller W. M., Müller U., Vögtle F., Pozzo J.-L., *Langmuir*, **2002**, *18*, 7096-7101.

André J.-C., Bouchy M., Lemaire J., Niclause M., *CR Acad. Sci.*, **1971**, *272*, 1192-1195.

André J.-C., A. Le Méhauté, O. de Witte, « *Dispositif pour réaliser un modèle de pièce industrielle* », FP 84-11241 du 16-07-**1984**.

André J.-C., Viriot M.-L., Villermaux J., *Pure Appl. Chem.*, **1986**, *58*, 907-916.

André J.-C., Cabrera M., Karrer P., **1990**, Patent WO 9006540 A1 19900614.

Armaroli N., Accorsi G., Holler M., Moudam O., Nierengarten J.-F., Zhou Z., Wegh R. T., Welter R., *Adv. Mater.*, **2006**, *18*, 1313–1316 (**147** citations).

Aubry J.-M., *J. Amer. Chem. Soc.*, **1985**, *107*, 5844-5849.

Baillet G., Giusti G., Guglielmetti R., *J. Photochem. Photobiol. A Chem.*, **1993**, *70*, 157-161 (**64** citations).

Barrejón M., Vizuete M., Gómez-Escalonilla M. J., Fierro J. L. G., Berlanga I., Zamora F., Abellán G., Atienzar P., Nierengarten J.-F., García H., Langa F., *Chem. Commun.*, **2014**, *50*, 9053-9055.

Bassani D. M., Darcos V., Mahony S., Desvergne J.-P., *J. Amer. Chem. Soc.*, **2000**, *122*, 8795-8796, (**66** citations).

Belotti D., Cossy J., Pete J.-P., Portella C., *Tetrahedron Lett.*, **1985**, *26*, 4591-4594.

Benchekroun-Mounir N., Dugat D., Gramain J.-C., Husson H.-P., *J. Org. Chem.*, **1993**, *58*, 6457-6465.

Bergeat A., Onvlee J., Naulin C., van der Avoird A., Costes M., *Nature Chem.*, **2015**, *7*, 349-353.

Bernaconi C., Cottier L., Descotes G., Praly J.-P., Rémy G., Grenier-Loustalot M.-F., Métras F., *Carbohydrate Res.*, **1983**, *115*, 105-116.

Berthet J., Micheau J.-C., Vermeeersch G., Delbaere S., *Tetrahedron Lett.*, **2006**, *47*, 2485- 2488.

Bertsch A., Jézéquel J.-Y., André, J.-C., *J. Photochem. Photobiol. A Chem.*, **1997a**, *107*, 275-281 (**43** citations).

Bertsch A., Zissi S., Jézéquel J.-Y., Corbel S., André J.-C., *Microsyst. Technology*, **1997b**, *3*, 42-47 (**90** citations).

Bideau M., Claudel B., Dubien C., Faure L., Kazouan H., *J. Photochem. Photobiol. A Chem.*, **1995**, *91*,137-1440.

Blanc S., Pigot T., Cugnet C., Brown R., Lacombe S., *PhysChemChemPhys*, **2010,** *12*, 11280-11290.

Blanchard-Desce M., *EPA NL*, **2013**, *85-86*, 27-35.

Bleuzen, A., Marvaud, V., Mathonière C., Sieklucka B., Verdaguer M., *Inorg. Chem.*, **2009**, *48*, 3453-3466.

Bois F., Gardette D., Gramain J.-C., *Tetrahedron Lett.*, **2004**, *41*, 8769-8772.

Bonnier, J.-M., Jardon, P. *J.Chim. Phys. Physico-Chim. Biol.*, **1972**, *69*, 245-248.

Bonneau R., Faure J., Joussot-Dubien J., *Chem. Phys. Lett.*, **1968**, *2*, 65-67.

Bonneau R., Joussot-Dubien J., Bensasson R., *Chem. Phys. Lett.*, **1969**, *3*, 353-356.

Bonneau R., Joussot-Dubien J., Salem L., Yarwood A. J., *J. Amer. Chem. Soc.*, **1976**, *98*, 4329-4330.

Bouas-Laurent H., Castellan A., Desvergne J.-P., Dumartin G., Courseille C., Gaultier J., Hauw C., *JCS Chem. Comm.*, **1972**, 1267-1268.

Bouas-Laurent H., Castellan A., Desvergne J.-P., *Pure Appl. Chem.*, **1980**, *52*, 2633-2648 (**223** citations).

Bouas-Laurent H., *EPA NL*, **1998**, *62*, 23-32. « A tribute to Jacques Joussot-Dubien » ; *EPA NL*, **2009**, *80*, 17-18 (Obituary) ; *L'Act. Chim.*, **2009**, *336*, 62-63 (homage article).

Bouas-Laurent H., Castellan A., Daney M., Desvergne J.-P., Guinand G., Marsau P., Riffaud M.-H., *J. Amer. Chem. Soc.*, **1986**, *108*, 315–317 (**106** citations).

Bouas-Laurent H., Castellan A., Desvergne J.-P., Lapouyade R., *Chem. Soc. Rev.*, **2000**, *29*, 43-55 (**252** citations) et **2001**, *30*, 248-263 (**184** citations).

Bouas-Laurent H., Dürr H., *Pure Appl. Chem.*, **2001**, *73*, 639-665 (**500** citations).

Bouas-Laurent, Desvergne J.-P., Bassani D. M., *EPA NL*, **2008**, *78*, 70-79 (a tribute to R. Bonneau).

Boule P., Othmen K., Richard C., Szczepanik B., Grabner G., *Inter. J. Photoenergy*, **1999**, *1*, 49-54.

Bousseksou A., Molnár G., Matouzenko G., *Eur. J. Inorg. Chem.*, **2004**, 4353-4369 (**107** citations).

Boyer D., Mahiou R., Franville A. C., Canet J.-L., Gautier A., Adumeau P., Deloncle R., Deschamps J., European Patent EP 25785816-A1, n° 12187378.0-2.05/10/**2012.**

Cadas J.-P., Rousset A., Lochet R., Courpron C., *C. R. Acad. Sci.*, **1962**, *254*, 2490-2494.

Cadet J., Sage E., Douki T., *Mutation Research-Fundamental Molecular Mechanisms of Mutagenesis*, **2005**, *571*, 3-17 (**394** citations).

Calas R., Lalande R., *Bull. Soc. Fr.*, **1959**, 763-769 and 770-772.

Cano-Yala H., Deronzier A., *J. Chem. Soc. Perkin 2*, **1984**, 1093-1098 (**72** citations).

Cantau C., Pigot T., Brown R., Mocho P., Maurette M.-T., Benoit-Marquié F., Lacombe S., *Appl. Catal. B : Environ.*, **2006**, *65*, 77- 85.

Caralp F., Foucher V., Lesclaux R., Wallington T. J., Hurley M. D., *PhysChemChemPhys*, **1999**, *1*, 3509-3517.

Cardy H., Poquet E., *Tetrahedron*, **1981**, *37*, 2279-2286.

Cardy H., Chevaldonnet C., Sainte-Cluque R., Poquet E., *Chem. Phys.*, **1985**, *94*, 385-395.

Castellan A., Colombo N., Nourmamode A., Zhu J., Lachenal D., Davidson R. S., Dunn L., J. *Wood & Technol.*, **1990**, *10*, 461-493 (**63** citations).

Castellan A., Grelier S., "Lignocellulosic Fibers and Wood Handbook, Renewable Materials for Today's Environment", Naceur M., Pizzi B., and A., Eds, Hoboken, New Jersey, J. Wiley and Sons, **2016**, chapter 21.

Cauquis G., Reverdy G., *Tetrahedron Lett.*, **1967**, 1493-1497

Cazeau-Dubroca C., Ait Lyazidi , Cambou P., Peirigua A., Cazeau P., Pesquer M., *J. Phys. Chem.*, **1989**, *93*, 2347-2358.

Cermenati L., Pichat P., Guillard C., Albini A., *J. Phys. Chem.*, **1997**, *101*, 2650-2658.

Chambon S., Manceau M., Fion M., Croo S., Rivaton A., Gardette J.-L., *Polymer*, **2008**, *49*, 3288-3294.

Cheldeville S., Kalugina Y., van de Meerakker S. Y. T., Naulin C., Lique F., Costes M., *Science*, **2013**, *341*, 1094-1096.

Collin J.-P., Laemmel A. C., Sauvage J.-P., *New J. Chem.*, **2001**, *25,* 22-24.

Collins R. T., Slaoui A., *MRS Bulletin*, **2007**, *32*, 211-218.

Coqueret X., Hajaiej A., Lablache-Combier A., Loucheux C., Mercier R., Pouliquen L., Randrianarisoa-Ramanantsoa L., *Pure Appl. Chem.*, **1990**, *62*, 1603-1614.

Cosnier S., Deronzier A., Moutet J.C., *J. Phys. Chem.*, **1985**, *89*, 4895-4877.

Couture A., Dubiez R., Lablache-Combier A., *J. Org. Chem.*, **1984**, *49*, 714-717.

Daniel C., Benard M., Dedieu A., Wiest R., Veillard A., *J. Phys. Chem.*, **1984**, *88*, 4805-4811.

Danion A., Disdier J., Guillard C., Abdelmalek F., Jaffrezic-Renault N., *Appl. Catal. B. : Environ.*, **2004**, *52-3*, 213-223.

Daudel R., cofounder at Menton in **1967** with Pullman B., Löwdin P.-O., Parr R. G. and Pople J. A. of the "International Academy of Molecular Quantum Sciences".

De Backer M., Lepoutre G., Sauvage F. X., *CR Acad. Sci. Série II*, **1983**, *296*, 185-188.

Decker C., *Prog. Polymer Sci.*, **1996**, *21*, 593-650 (**360** citations).

Decreau R., Chanon M., Julliard M., *Inorg. Chim. Acta*, **1999**, *293*, 80-87.

Delbaere S., Micheau J.-C., Vermeersch G., *Org. Lett.*, **2002**, *18*, 3143-3145.

Del Guerzo A., *EPA NL*, **2013**, *85-86*, 36-40.

Delort A.-M., Mailhot G., Deguillaume L., *L'Act. Chim.*, **2015**, *395*, 14-17.

Deronzier A., *Tetrahedron Lett.,* **1984**, *25*, 2867-2868.

Deshayes H., Pete J.-P., Portella C., Scholler D., *JCS Chem. Commun.*, **1975**, 439-440.

Desvergne J.-P., Bouas-Laurent H., Lapouyade R., Gaultier J., Hauv C., Dupuy F., *Mol. Cryst. Liq. Cryst.*, **1972**, *19*, 63-85.

Desvergne J.-P., Thomas J. M., Williams J. O., Bouas-Laurent H., *J. Chem. Soc. Perkin 2*, **1974**, 363-368.

Desvergne J.-P., Bouas-Laurent H., *Chem. Commun.*, **1978**, 403-404.

Desvergne J-P., Fages F., Bouas-Laurent H., Marsau P., *Pure Appl. Chem.*, **1992**, *64*, 1231-1238.

Desvergne J.-P., Perez-Inestrosa E., Bouas-Laurent H., Jonusauskas G., Oberlé J., Rullière C., in « Fluorescence Spectroscopy-Methods and Applications » ed. B. Valeur & J.C. Brochon, Springer-Verlag, Berlin, **2001**, chap. 8, 157-159.

Desvergne J.-P., Olive A. G. L., Sangeetha N. M. , Reichwagen J., Hopf H., Del Guerzo A., *Pure Appl. Chem.*, **2006**, *78*, 2333-2339.

De Waele V., Buntinx G., Poizat O., Flament J.-P., Kassab E., *J. Chem. Phys.*, **1999**, *10*, 6353-6364.

Dietrich-Buchecker C., Gaviña P., Jimenez-Molero M. C., Sauvage J.-P., *Acc. Chem. Res.*, **2001,** *34*, 477–487 (**506** citations).

Dorthe G., Costes M., Naulin C., Joussot-Dubien J., Vaucamps C., Nouchi G., *J. Chem. Phys.*, **1985**, *83*, 3171-3172.

Douki T., Rebelo-Moreira S., Hamon N., Bayle P.-A., *Org. Lett.*, **2015**, *17*, 246-249.

Dumas S., Leprêtre, J. C., Lepellec A., Darmanyan A., Jardon P., *J. Photochem. Photobiol. A Chem.*, **2004**, *163*, 297-306.

Dumon P., Jonusauskas G., Dupuy F., Pée P., Rullière C., Létard J.-F., Lapouyade R., *J. Phys. Chem.*, **1994**, *98*, 10391-10396.

Dumont E., Wibowo, M., Roca-Sanjuán D., Garavelli M., Assfeld X., Monari A., *J. Phys. Chem. Lett.*, **2015**, *6*, 576-580.

Dupuy F., Pée P., Lalanne R., Lemaistre J. P., Vaucamps C., Port H., Kottis P., *Mol. Phys.*, **1978**, *35*, 595-99.

El Gemayel M., Börjesson K., Herder M., Duong D. T., Hutchison J. A., Ruzié C., Schweicher G., Salleo A., Geerts Y., Hecht S., Orgiu E., Samorì P., *Nature Comm.*, **2015**, 6, article n° 6330.

Ern J., Bens A.T., Martin H.-D., Mukamel S., Tratiak F., Tsyganenko K., Kuldova K., Trommsdorff H.P., Kryschi C., *J. Chem. Pys. A*, **2001**, *105*, 1741-1749 (**74** citations).

Faure J., *Pure Appl. Chem.*, **1977**, *49*, 487-494.

Fernández-Acebes A., Lehn J.-M., *Adv. Mater.*, **1998**, *10*, 1519-1522.

Fery-Forgues S., *Nanoscale*, **2013**, *5*, 8428-8442.

Figueira-Duarte T. M., Clifford J., Amendola V., Gégout A., Olivier J., Cardinali F., Meneghetti M., Armaroli N., Nierengarten J.-F., *Chem. Commun.*, **2006**, 2054-2056.

Fihri A., Artero V., Razavet M., Baffert C., Leibl W., Fontecave M., *Angew. Chem. Int. Ed.*, **2008**, *47*, 564-567.

Fornier de Violet P., Bonneau R., Lapouyade R., Koussini R., Ware W. R., *J. Amer. Chem. Soc.*, **1978**, *100*, 6683-6687.

Fouassier C., *L'Act. Chim.,* **2002**, mars, 98-101.

Fouassier J.-P., Lougnot D.-J., Paverne A., Wieder F., *Chem. Phys. Lett.*, **1987**, *135*, 30-34.

Franck-Neumann M., Lohmann J.-J., *Angew. Chem. Int. Ed. Engl.*, **1977**, *16*, 323-324.

Frochot C., Di Stasio B., Vanderesse R., Belgy M.-J., Dodeller M., Guillemin F., Viriot M.-L., Barberi-Heyob M., *Bioorg. Chem.*, **2007**, *35*, 205-220.

Frochot C. , Barberi-Heyob M. , Blanchard-Desce M., Bolotine L. , Bonneau S., Mauriello Jimenez C., Durand J.-O., Lassale H.-P., Lemercier G., Mordon S., Maillard P., Sol V., Vever-Bizet C., Vicendo P., *L'Actualité Chimique*, **2015**, *397-398*, 46-50.

Gaiduk A., Yorulmaz, Ruijgrok P. V., Orrit M., *Science*, **2010**, *330*, 353-356.

Gélis C., Girard S., Mavon A., Delverdier M., Paillous N., Vicendo P., *Photodermatol. Photoimmunol. Photomed.*, **2003**, *19*, 242-253.

Genin E., Gao Z., Varela J., Daniel J., Bsaibess T., Gosse I., Groc L., Cognet L., Blanchard-Desce M., *Adv. Mater.*, **2014**, *26*, 2258-2261.

Ghose A., Rebarz M., Maltsev O. V., Hintermann L., Ruckebusch C., Fron E., Hofkens J., Mély Y., Naumov P., Sliwa M., Didier P., *J. Phys. Chem. B.*, **2015**, *119*, 2638-2649.

Giansante C., Raffy G., Schäfer C., Rahma H., Kao M.-T., Olive A. G. L., Del Guerzo A., *J. Amer. Chem. Soc.*, **2011**, *133*, 316-325 (**70** citations).

Gicquel E., Paillous N., Vicendo P., *Photochem. Photobiol.*, **2000**, *72*, 583-589.

Gilat S. L., Kawai S. H., Lehn J.-M., *JCS, Chem. Commun.*, **1993**, 1439-1442.

Guillard C., Hermann J.-M., Chevrier J.-P., Bertrand C., Philibert E., Patent W.O. **2005**/097302.

Grichine A., Haefele A., Pascal S., Duperray A., Michel R., Andraud C., Maury O., *Chem. Sci.*, **2014**, **5**, 3475-3485.

Hamelin O., Guillo P., Loiseau F, Boissonnet M. F., Ménage S., *Inorg. Chem.*, **2011**, *50*, 7952-7954.

Hermann J.-M., Disdier J., Pichat P., *J. Phys. Chem.*, **1986**, *90*, 6028-6034.

Hoffmann N., Bertrand S., Marinković S., Pesch J., *Pure Appl. Chem.*, **2006**, *78*, 2227-2246.

Houas A., Lachheb H., Ksibi M., Alaoui E., Guillard C., Hermann J.-M., *Appl. Catalysis B-Environ.*, **2001**, *31*, 145-157 (**715** citations).

Huang C.-H., McClenaghan N. D., Kuhn A., Hofstraat J. W., Bassani D. M., *Org. Lett.*, **2005**, *7*, 3409-3412 (**84** citations).

Huron B., Malrieu J.-P., Rancurel P., *J. Chem. Phys.*, **1973**, *58*, 5745-5759 (**916** citations).

Ibrahim A., Ley C., Allonas X., Tarzi O.I., Chan Yong A., Carré C., Chevallier R., *Photochem. Photobiol. Sci.,* **2012**, *11,* 1682-1690.

Jacquemin D., Daniel C., *L'Act. Chim.*, **2014**, *382-383*, 93-99.

Jacques P., Allonas X., *J. Photochem. Photobiol. A Chem.*, **1994**, *78*, 1-5.

Joussot-Dubien J., Lesclaux R., *CR Acad. Sci.*, **1964**, *258*, 4260-4262.

Jubera V., Chaminade J.-P., Garcia A., Guillen F., Fouassier C., *J. Luminescence*, **2003**, *101*, 1-10 (**91** citations).

Jung A.-V., Frochot C., Parant S., Lartiges B. S., Selve C., Viriot M.-L., Bersillon J.-L., *Org. Geochem.*, **2005**, *36*, 1252-1271.

Kaptein R., *J. Chem. Soc. D*, *Chem. Commun.*, **1971**, 732-733.

Kartheuser B., Costarramone N., Pigot T., Lacombe S., *Environ. Sci. Poll. Res.*, **2012,** *19*, 3763-3771.

Keller V., Keller N., Lett M. C., Ledoux M. J., Patent W.O. 20066 1518, **2004.**

Khodja A. A., Sehili T., Pilichowski J.-F., Boule P., *J. Photochem. Photobiol. A Chem.*, **2001**, *141*, 231-239 (**357** citations).

Kirch M., Lehn J.-M., Sauvage J.-P., *Helv. Chim. Acta*, **1979**, *62*, 1345-1384.

Lablache-Combier A., *L'Act. Chim.*, **1973**, n°6, 6-14 ; n°7, 9-19.

Lacombe S., Soumillion J. P., El Kadib A., Pigot T., Blanc S., Brown R., Oliveros E., Cantau C., Saint-Cricq P.**,** *Langmuir***,** **2009,** *25*,11168-11179.

Lacoste J., Thérias S., *L'Act. Chim.*, **2015**, *395*, 38-43.

Lalevée J., Telitel S., Xiao P., Lepeltier M., Dumur F., Morlet-Savary F., Gigmes D., Fouassier J.-P., *Beilstein J. Org. Chem.*, **2014,** *10,* 863–876.

Lamotte M., Lesclaux R., Merle A.-M., Joussot-Dubien J., *Farad. Discus. Chem. Soc.*, **1974**, *58*, 253-260.

Lamotte M., Rima J., Garrigues P., Ewald M., Joussot-Dubien J., Pereyre J., in *Polynuclear Aromatic Hydrocarbons*, Cooke M. and Dennis A. J. eds, Battelle press, Columbus Ohio, **1984**, 785-798.

Lapouyade R., Czeschka K., Majenz N., Rettig W., Gilabert E., Rullière C., *J. Phys. Chem.*, **1992**, *96*, 9643-9650.

Lattes A., Oliveros E., Rivière M., Belzeck C., Mostowicz D., Abramskj W., Piccinni-Leopardi C., Germain G., Van Meerssche M., *J. Amer. Chem. Soc.*, **1982**, *104*, 3929-3934.

Lazare S., Granier V., *Laser Chem.*, **1989**, *10*, 25-40.

Legrini O., Oliveros E., Braun A., *Chem. Rev.*, **1993**, *93*, 671-698 (**1773** citations).

Lehn J.-M., Sauvage J.-P., *Nouv. J. Chim.*, **1977**, *1*, 449-451.

Lehn J.-M., Ziessel R., *J. Organomet. Chem.*, **1990**, *382*, 157-173.

Lehn J.-M. » *Supramolecular Chemistry, Concept and Perspectives* », **1995**, Wiley-VCH, Weinheim, pages 48, 78, 94-103 and 128-134 concern photochemistry.

Lemaire J., *Pure Appl. Chem.*, **1982**, *54*, 1667-1682.

Lerner D. A., Ricchiero F. R., Giannotti C., Maillard P., *J. Photochem.*, **1982**, *18*, 193 -196.

Lesclaux R., Joussot-Dubien J., *J. Chim. Phys.*, **1964**, *61*, 1147-1152.

Lesclaux R., Joussot-Dubien J., *CR Acad. Sci.*, **1966**, *263*, 1177-1180.

Létard J.-F., Guionneau, Codjovi E., Lavastre O., Bravic G., Chasseau D., Kahn O., *J. Amer. Chem. Soc.*, **1997**, *119*, 10861-10862.

Ley C., Christmann J., Ibrahim A., Di Stefano L. H., Allonas X., *Beilstein J. Org. Chem.*, **2014**, *10*, 936-947.

Leydet Y., Bassani D. M., Jonusauskas G., McClenaghan N. D., *J. Amer. Chem. Soc.*, **2007**, *129*, 8688-8689. *Nathan McClenaghan was awarded in 2008 a prestigious ERC "Young Investigators Starting Grant".*

Liatard S., Chauvin J., Balestro F., Jouvenot D., Loiseau F., Deronzier A., *J. Phys. Chem. C.*, **2013**, *117*, 20431-20439.

Lin Y., Ferronato C., Deng N., Wu F., Chovelon J.-M., *Appl. Catal. B*, **2009**, *88*, 32-41.

Loustauneau P., Nouchi G., Rousset A., *C. R. Acad. Sci.*, **1963**, *257*, 2928-2932.

Malaval J.-P., Chaimbault C., Fisher B., Morand J.-P., Lapouyade R., *Res. Chem. Intermed.*, **2001**, *27*, 21-34.

Malrieu J.-P., Nebot-Gil I., Sánchez-Marín J., *Pure Appl. Chem.*, **1984**, *56*, 1241-1254.

Marko J., Vermeersch G., Febvay-Garot N., Caplain S., Lablache-Combier A., *Photochem. Photobiol.*, **1983**, *38*, 169-175.

Mauro M., Aliprandi A., Septiadi D., Kehr N. S., De Cola L., *Chem. Soc. Rev.*, **2014a**, *43*, 4144-4166.

Mauro M., Aliprandi A., Cebrián C., Wang D., Kübel C., De Cola L., *Chem. Commun.*, **2014b**, *50*, 7269-7272.

Maus M., Rettig W., Bonnafous D., Lapouyade R., *J. Phys. Chem. A*, **1999**, *103*, 3388-3401.

Moine B., Bizarri G., *Opt. Mat.*, **2006**, *28*, 587-591.

Monneyron P., de la Guardia A., Manero M. H., Oliveros E., Maurette M.-T., Benoit-Marquié F., *Int. J. Photoenergy*, **2003**, *5*, 167-174.

Mousseron M., *Pure Appl. Chem.*, **1964**, *9*, 481-492.

Moutet J.-C., Reverdy G., *JCS Chem. Commun.*, **1982**, 654-655.

Muzart J., Pete J.-P., *Chem. Commun.*, **1980**, 257- 258.

Nardello V., Azaroual N., Cervoise I., Vermeersch G., Aubry J.-M., *Tetrahedron*, **1996**, *52*, 2031-2046.

Oliveros E., Rivière M., Malrieu J. P., Teichteil C., *J. Am. Chem. Soc.*, **1979**, *101*, 318-322.

Orgiu E., Samorí P., *Adv. Mater.*, **2014**, *26*, 1827-1845.

Orrit M., Bernard J., *Phys. Rev. Lett.*, **1990**, *65*, 2716-2719.

Percherancier J.-P., Chapelon R., Pouyet B., *J. Photochem. Photobiol. A Chem.*, **1995**, *87*, 261-266 (**64** citations).

Pete J.-P., Hénin F., Mortezaei R., Muzart J., Piva O., *Pure Appl. Chem.*, **1986**, *58*, 1257-1262.

Pete J.-P., *Adv. Photochem.*, **1996**, *21*, 135-216.

Petrier C., Dupuy C., Jardon P., Gautron R., *Nouv. J. Chim.*, **1982**, *6*, 495-503.

Pichat P., dans « Chemical Degradation. Methods for wastes and pollutants : environment and industrial applications » Tarr M. A. (ed.), Marcel Dekker, New-York, **2003**, 77-119.

Pichat P., Enriquez R., Mietton E., *Solid State Phenom.*, **2010**,*162*, 41-48.

Pichat P., *Appl. Catal.B*, **2010**, *99*, 428–434.

Pichat P., Self-cleaning materials based on solar photocatalysis in "New and future developments in catalysis", Vol. 7 "Solar catalysis", ed. S.L. Suib, Elsevier, pp. 167-190, **2013**.

Pichat P., *Molecules*, **2014**, 19, 15075-15087.

Picot A. , D'Aléo A., Baldeck P. L., Grichine A., Duperray A., Andraud C. , Maury O., *J. Amer. Chem. Soc.*, **2008**, *130*, 1532-1533 (**149** citations).

Pignatello J. J., Oliveros E., Mackay A., *Crit. Rev. Env. Sci. Technol.*, **2006**, *36*, 1-84 (**406** citations en 2012).

Portella C., Pete J.-P., *Tetrahedron Lett.*, **1985**, *26*, 211-214.

Raoult S., Rayez M.-T., J.-C. Rayez, Lesclaux R., *Phys. Chem. Chem. Phys.*, **2004**, *6*, 2245-2253.

Reisch A., Didier P., Richert L., Oncul S., Arntz Y., Mély Y., Klymchenko A. S., *Nature Commun.*, **2014**, *5*, n°4089.

Renaud C., Mougnier S.-J., Pavlopoulou E., Brochon C., Fleury G., Deribew D., Portale G., Cloutet E., Chambon S., Vignau L., Hadziioannou G., *Adv. Mater.*, **2012**, *24*, 2196-2201.

Rico I., Maurette M.-T., Oliveros E., Rivière M., Lattes A., *Tetrahedron Lett.*, **1978**, 4795-4798.

Ronzani F., Trivella A., Arzoumanian E., Blanc S., Sarakha M., Richard C., Oliveros E., Lacombe S., *Photochem. Photobiol. Sci.,* **2013**, *12*, 2160-2169.

Rullière C., ed., "Femtosecond Laser Pulses, Principle and Experiments", Springer, Berlin, 2001, 2nd ed. 2005.

Ruyffelaere F., Marteau C., Nardello-Rataj V., Favier D., Vezin H., Aubry J.-M., *Flavour Fragrance J.*, **2013**, *28*, 316-326.

Saimov S., Ecoffet C., Lougnot D.-J., *J. Mater. Sci.-Mater. in Electronics*, **2003**, *14*, 855-856.

Samat A., Lokshin V., Chamontin K., Levi D., Pepe G., Guglielmetti R., *Tetrahedron*, **2001**, *57*, 7349-7359 (**48** citations).

Sandorfy C., Lussier L. S., Richer G., Goursot A., Pénigault E., Weber J., *J. Mol. Struct.*, **1986,** *141*, 1-12.

Sauvage J.-P., Collin J.-P., Chambron J.-C., Guillerez S., Coudret C., Balzani V., Barigelletti F., De Cola L., Flamigni L., *Chem. Rev.*, **1994**, *94*, 993-1019 (**1204** citations).

Sauvage J.-P., *Acc. Chem. Res.*, **1998**, *31*, 611-619 (**656** citations).

Schmidt R., Tanielian C., Dunsbach R., Wolff C., *J. Photochem. Photobiol. A Chem.*, **1994**, *79*, 11-17.

Schuster D., Bonneau R., Dunn D. A., Rao J. M., Joussot-Dubien J., *J. Amer. Chem. Soc.*, **1984**, *106*, 2706-2707.

Serpone N., Maruthamuthu P., Pichat P., Pelizetti E., Hidaka H., *J. Photochem. Photobiol. A Chem.*, **1995**, *85*, 247-255 (**424** citations).

Seta P., Bienvenue E., Moore A. L., Mathis P., Bensasson R. V., Liddell P., Pessiki P. J., Joy A., Moore T. A., Gust D., *Nature*, **1985**, *316*, 653- 655.

Sliwa M., Mouton N., Ruckebusch C., Poisson L., Idrissi A., Aloïse S., Potier L., Dubois J., Poizat O., Buntinx G., *Photochem. Photobiol. Sci.*, **2010**, *9*, 661-669.

Stalmach U., de Boer B., Videlot C., van Hutten P. F., Hadziioannou G., *J. Amer. Chem. Soc.*, **2000**, *122*, 5464-6472 (**266** citations).

Stoll T., Gennari M., Fortage J., Castillo C. E., Rebarz M., Sliwa M., Poizat O., Odobel F., Deronzier A., Collomb M.-N., *Angew. Chem. Int. Ed.*, **2014**, *53*, 1654-1658.

Streith J., Sigwalt C., *Tetrahedron Lett.*, **1966**, *13*, 1347-1351.

Streith J., *Pure Appl. Chem.,* **1977**, *49*, 305-315.

Szalóki G., Sevez G., Berthet J., Pozzo J.-L., Delbaere S., *J. Amer. Chem. Soc.*, **2014**, *136*, 13510-13513.

Tanielian C., Wolff C., Esch M., *J. Phys. Chem.*, **1996**, *100*, 6555-6560.

Tanielian C., Méchin R., Segrouchni R., Schweitzer C., *Photochem. Photobiol.*, **2000**, *71*, 12-19.

Tanielian C., Schweitzer C., Segrouchni R., Esch M., Méchin R., *Photochem. Photobiol. Sci.*, **2003**, *2*, 297-305.

Teulade-Fichou M.-P., Perrin D., Boutorine A., Polverari D., Vigneron J. P., Lehn J.-M., Sun J. S., Garestier I., Hélène C., *J. Amer. Chem. Soc.*, **2001**, *123*, 9283-9292.

Thakur A. K., Wantz G., Garcia-Belmonte G., Bisquert J., Hirsch L., *Solar Energy Materials and Solar Cells*, **2011**, *95*, 2131-2135.

Trommsdorff H. P., Corval A., von Laue L., *Pure Appl. Chem.*, **1995**, *67*, 191-199.

Tron A., Jacquot de Rouville H.-P., Ducrot A., Tucker J. H. R., Baroncini M., Credi A., McClenaghan N. D., *Chem. Commun.*, **2015a**, *51*, 2810-2813.

Tron A., Thornton P. J., Lincheneau C., Desvergne J.-P., Spencer N., Tucker J. H. R., McClenaghan N. D., *J. Org. Chem.*, **2015b**, *80*, 988-996.

Uddin M. T., Nicolas Y., Olivier C., Toupance T., Servant L., Müller M. M., Kleebe H.-J., Ziegler J., Jaegermann, *Inorg. Chem.*, **2012**, *51*, 7764-7773.

Ulrich G., Goze C., Guardigli M., Roda A., Ziessel R., *Angew. Chem. Int. Ed.*, **2005**, *44*, 3694-3698 (**117** citations).

Vaillant O., El Cheikh K., Warther D., Brevet D., Maynadier M., Bouffard E., Salgues F., Jeanjean A., Puche P., Mazerolles C., Maillard P., Mongin O., Blanchard-Desce M., Raehm L., Rébillard X., Durand J. O., Gary-Bobo M., Morère A., Garcia M., *Angew. Chem. Int. Ed.*, **2015**, *54*, 5952-5956.

Veyret B., Lesclaux R., Rayez M.- T., Rayez J.- C., Cox R. A., Moortgat G.K., *J. Phys. Chem.*, **1989**, *93*, 2368–2374 (**103** citations).

Viriot M.-L., Guillemin F., Barberi-Heyob M., *Trends in Biotechnology (nanoparticles)*, **2008**, *26*, 612-621 (245 citations).

Vockler S., Macfarlane R.M., Genack A. Z., Trommsdorff H. P., van der Waals J. H., *J. Chem. Phys.*, **1977**, *67*, 1759-1765 (**96** citations).

Xiao P., Dumur F., Graff B., Zhang J., Morlet-Savary F., Gigmes D., Fouassier J.-P., Lalevée J., *J. Polymer Sci., Part A : Polymer Chem.*, **2015**, *53*, 567-575.

Zhang Y. Z., Ferko P., Siretanu D., Abakei R., Rath N. P., Shaw M. J., Clérac R., Mathonière C., *J. Amer. Chem. Soc.*, **2014**, *136*, 16854-16864.

Zyss J., Nicoud J.-F., Coquillay M., *J. Chem. Phys.*, **1984**, *81*, 4160-4167 (**440** citations).

Acronyms

AFM : atomic force microscopy
Atochimie : Aquitaine Total Organico chemistry
CEA : Commissariat à l'Energie Atomique
CEISAM : Chimie et interdisciplinarité, Synthèse, Analyse, Modélisation
CGE: Compagnie Générale d'Electricité
CHU : Centre Hospitalier Universitaire
CIDNP : Chemically Induced Dynamic Nuclear Polarization
CMOA : Centre de Mécanique ondulatoire Appliquée
CNAM : Conservatoire des Arts et Métiers
CNEP : Centre National d'Evaluation de Photoprotection
CNET : Centre National d'Etudes des Télécommunications
CNRS : Centre National de la Recherche Scientifique
COMEX : Collisions Moléculaires en Milieux Extrêmes
CRPP : Centre de Recherches Paul Pascal
DNA : Deoxyribonucleic acid
DSC : Differential Scanning Calorimetry
EDF: Electricité De France
ENS : Ecole Normale Supérieure, rue d'Ulm Paris
ENSIC : Ecole Nationale Supérieure des Industries Chimiques
ENSSAT : Ecole Nationale Supérieure des Sciences Appliquées et de Technologie
ENSCP : Ecole Nationale Supérieure de Chimie de Paris, Paris-Tech
ENSCM : Ecole Nationale Supérieure de Chimie de Montpellier
EPA : European photochemistry Association
ESP : European Society for Photobiology
ESPCI : Ecole Supérieure de Physique et Chimie Industrielle, Paris
GDR : Groupe de Recherche
GFCP : Groupe Français de Cinétique et Photochimie
GFP : Groupe Français de Photochimie
GFP2P : Goupe Français de Photochimie, Photophysique et Photosciences
IBM : International Business Machines Corporation
ICMCB : Institut de Chimie de la Matière Condensée de Bordeaux
ICMMO : Institut de Chimie des Molécules et Matériaux d'Orsay
ICP: International Conference on Photochemistry

IMRCP : Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique
IMS : Intégration du Matériau au Système
INAC : Institut des Nanosciences et Cryogénie INSERM : Institut National de la Santé et de la Recherche Médicale
IR : Infrared
IRCEL : Institut de Recherche sur la Catalyse et l'Environnement de Lyon
ISIS : Institut de Science et d'Ingénierie Supramoléculaire
ISM : Institut des Sciences Moléculaires
IS2M : Institut de Sciences des Matériaux de Mulhouse
ISMO : Institut des Sciences Moléculaires
ISOP : International Symposium on Photochromism
ISyEB : Institut de Systématique, Evolution, Biodiversité
ITER : International Thermonuclear Experimental Reactor
ITODYS : Interfaces, Traitements, Organisation et Dynamique des Systèmes
IUPAC : International Union of Pure and Applied Chemistry
LASIR : Laboratoire de Spectroscopie Infrarouge et Raman
LCPO : Laboratoire de chimie des Polymères Organiques
LERMA : Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères
LERMAB : Laboratoire d'Etude et de Recherche sur le Matériau Bois
Lidyl : Laboratoire des interactions, dynamique et laser
LPTC : Laboratoire de Physico Toxicochimie des Systèmes Naturels
LURE : Laboratoire pour l'utilisation du rayonnement électromagnétique
LPPM: Laboratory of Molecular Photophysics
MNHN : Museum National d'Histoire Naturelle
NEO : Nanostructures Organiques
NIMBE: Nanosciences et Innovation pour les Matériaux, la Biomédecine, l'Energie
NLO: non linear optics
OLED : Organic Light ElectroLuminescent
NMR : Nuclear Magnetic Resonance
OPV : organic photovoltaic
PPG Industry : Pittsburgh Plate Glass, USA
PPS: Photochemical and Photobiological Sciences
PPSM : Laboratoire de Photophysique et de Photochimie Supramoléculaire et Macromoléculaire

RNA: ribonucleic acid
SFPb : French Society for Photobiology
SFPD : Société Française de PhotoDermatologie
SNPE : Société des Poudres et Explosifs
UCLA : University of California, Los Angeles
UPMC : Université Pierre et Marie Curie or Paris 6
V-UV : vacuum ultraviolet

List of Researchers

The names refer to the introduction (I) or the different headings and the references (ref)

Aimé Jean-Pierre: Bordeaux Physics
Allonas Xavier : Mulhouse, ref. Jacques 1994, Ley 2014.
André Jean-Claude : Nancy, ref. 1971, 1984, 1986, 1990, Ba, Cj, Bertsch 1997a, Bertsch 1997b.
Andraud Chantal: Lyon ENS, ref. 2015, Picot 2008,
Arnaud René : Clermont-Ferrand, Ba
Artero Vincent : Grenoble, ref. Fihri 2008
Aubard Jean : Marseille, Paris VII
Aubry Jean-Marie : Lille, ref. 1985, Nardello 1996, Ruyffelaere 2013
Baba Mohamed : Clermont-Ferrand
Backov Rénal : Bordeaux, Pau
Baldeck Patrice : Grenoble, ref. Picot 2008, Andraud 2015
Barberi-Heyob Muriel : Nancy, ref. Frochot 2007, 2015, Viriot 2008
Bassani Dario : I, Bordeaux, ref. 2000, Huang 2005, Leydet 2007, Bouas-Laurent 2008, D d, E c, o.
Bensasson René: Paris MNHN, Orsay, Bordeaux, ref. 1971, Amand 1975, Bonneau 1969, Moore 1984, Quaranta 2014, Seta 1985, D c
Bergeat Astrid: Bordeaux, ref 2015
Bigot Jean-Yves: Strasbourg
Blanchard-Desce Mireille: Rennes, Bordeaux, ref. 2013, 2015, Mongin 2002, Katan 2005, Genin 2014, Frochot 2015, Vaillant 2015
Blanchi Jean-Pierre: Grenoble U. Joseph Fourier
Bleuzen Anne: Orsay ICMMO, Bordeaux, ref. 2009
Bolte Michèle : Clermont-Ferrand, ref. Bb
Bonneau Roland : I, Bordeaux, ref. 1968, 1969, 1976, Fornier de Violet 1978, Schuster 1984, Bouas-Laurent 2008, E l, Fa,b, II

Bonnier Jane-Marie : Grenoble, ref. 1972
Bouas-Laurent Henri : I, Bordeaux, A a,
B a, C h, E b, F c, EPA, ref. 1972,1980,1986, 1998, 2000, 2001, 2008, 2009, Desvergne 1974, 1978, 1992
Bouchy Michel : Nancy, ref. André 1971
Boule Pierre : Clermont-Ferrand, ref. 1999, Khodja 2001
Bousquet Jean-Alain : Mulhouse
Bousseksou Azzedine : Toulouse, ref. 2004
Braun André : Mulhouse, Toulouse, ref. Legrini 1993, Ci
Brochon Cyril: Bordeaux, Renaud 2012
Brown Ross : Bordeaux, Bordeaux Physics, Pau, ref. Cantau 2006, Lacombe 2009, Blanc 2010
Buntinx Guy : Lille, ref. De Waele 1999, Poisson 2006, Sliwa 2010
Cadet Jean : Grenoble, ref. 2005, Da
Calas Raymond : Bordeaux, ref. 1959
Cantau Christophe : Pau, ref. 2006, Lacombe 2009
Caplain Serge : Lille, ref. Marko 1983
Caralp Françoise : Bordeaux, ref. 1999
Cardy Henri : Pau, ref. 1981, 1985
Carré Christiane : Brest, Mulhouse, ref. Ibrahim 2012
Catteau Jean-Pierre : Lille
Castellan Alain : Bordeaux, B a, ref. 1990, 2016, Bouas-Laurent 1972, Bouas-Laurent 1980, Bouas-Laurent 1986, Bouas-Laurent 2000 and 2001
Castellano Azélio : Lille
Cazeau-Dubroca Claudie: Bordeaux Physics, ref 1989
Chabrat Jean-Pierre: Bordeaux Physics
Chaillet Marc : Pau
Chanon Michel : Marseille, ref. Cd, Cm,
Chambron Jean-Claude : Strasbourg, ref. Sauvage 1994
Chauvet Jean-Paul: Lyon Ecole Centrale
Chauvin Jérôme : Grenoble, ref. Liatard 2013
Chovelon Jean-Marc : Lyon, ref. Bb, Lin 2009.
Claudel Bernard : Lyon INSA, ref. Bideau 1995
Claeys Wilfrid: Bordeaux Physics
Clérac Rodolphe : Bordeaux, ref. Zhang 2014
Cloutet Eric: Bordeaux, Renaud 2012
Cognet Laurent: Bordeaux Physics
Collin Jean-Paul: Strasbourg, ref. 2001, Sauvage 1994
Collomb Marie-Noëlle : Grenoble, ref. Stoll 2014

Cossy Janine : Paris ESPCI, Reims, ref. Belotti 1985
Costes Michel : Bordeaux, Bergeat 2015, Cheldeville 2013, Dorthe 1985
Coudret: Toulouse
Couture Axel : Lille, ref. 1984.
Couturier-Tamburelli Isabelle : Marseille, ref. Bc, XV-XIX
Daniel Chantal : Nantes, Strasbourg, ref. 1984, Jacquemin 2014
Dantelle Géraldine : Grenoble
Dargelos Alain : Pau
Debaere : Lille
De Backer : Lille, ref. 1983
De Cola Luisa : Strasbourg, ref. Sauvage 1994, Mauro 2014a and 2014b, D d
Decker Christian : Mulhouse, ref. 1996
Dedieu Alain : Strasbourg, ref. Daniel 1984
Déglise Xavier : Nancy, ref. B a
Del Guerzo André: Bordeaux, ref. 2013, Giansante 2011, E c.
Deflandre André : Clermont-Ferrand
Deguillaume Laurent : Clermont-Ferrand, ref. Delort 2015
Delort Anne-Marie : Clermont-Ferrand, ref. 2015
Delville Jean-Pierre: Bordeaux Physics
Demortier Antoine : Lille
Deronzier Alain : Grenoble, ref. 1984, Cano-Yelo 1984, Cosnier 1985, Liatard 2013, Stoll 2014,
Deschamps Jean : Pau, ref. 2012
Descotes Gérard : Lyon, ref. Bernaconi 1983
Desvergne Jean-Pierre : Cachan ENS, Bordeaux, ref. 1972, 1974, 1978, 1992, Bouas-Laurent 1972, Bouas-Laurent 1980, Bouas-Laurent 1986, Bassani 2000, Bouas-Laurent 2000 et 2001, Bouas-Laurent 2008, Tron 2015b, D b, E h
Deumié Michel : Perpignan
Devolder Pascal : Lille
Dietrich-Buchecker Christiane: Strasbourg, ref. 2001
Dixon Isabelle : Toulouse
Dorthe Gérard : Bordeaux, ref. 1985
Doucet Henri : Rennes, Nantes, ref. Kedong 2014,
Douki Thierry : I, Grenoble, SFPb , ref. 2015, Cadet 2005, Markovitsi 2007, Vaya 2010, Da
Ducasse André: Bordeaux Physics
Dujardin Christophe : Lyon, Df

Dumont Elise : Lyon, ref. 2015
Dupuy François: Bordeaux Physics, ref Desvergne 1972
Durand Jean-Olivier : Montpellier, ref. Frochot 2015, Vaillant 2015
Ecoffet Carole : Mulhouse, ref. Lalevée 2014, Saimov 2003
Ewald Marc: Bordeaux, Lamotte 1984
Eymann Jean-Octave : Mulhouse
Fages Frédéric : Angers, Bordeaux, Marseille, ref. Desvergne 1992, Ahmed 2002
Faure Jean : I, Bordeaux, Mulhouse, Orsay, Cachan, ref. 1977, Bonneau 1968, A c, E k
Fery-Forgues Suzanne : Toulouse, ref. 2013,
Fleury Guillaume: Bordeaux, Renaud 2012
Fleury Jean-Pierre : Mulhouse
Fontecave Marc: Grenoble, ref. Fihri 2008,
Fouassier Claude : Bordeaux, ref. 2002, Jubera 2003
Fouassier Jean-Pierre: Mulhouse, ref. 1987, 2014, Cf, Ck, Cl, Saimov 2003, Xiao 2015
Franck-Neumann Michel: Strasbourg, ref. 1977
Freysz Eric: Bordeaux Physics
Frochot Céline : I, Nancy, ref. 2007, 2015, Jung 2005, Bb
Gardette Jean-Luc : Clermont-Ferrand, Be, Chambon 2008
Garrigues Philippe : Bordeaux, ref. Lamotte 1984
Gautron René : Grenoble, Marseille, ref. Petrier 1982
Gilat Sylvain : Strasbourg, ref. 1993
Giusti Gérard: Marseille, ref. Baillet 1993
Gonbeau Danielle : Pau
Goudmand Pierre : Lille, Tableau A
Goumet Guy: Bordeaux Physics
Goursot Annick : Mulhouse, ref. Sandorfy 1986
Graff Bernadette : Mulhouse, ref. Xiao 2015
Gramain Jean-Claude : Clermont-Ferrand, Be, ref. Bois 2004
Grandclaudon Pierre : Lille
Grelier Stéphane : Bordeaux, ref. Castellan 2016
Grivet Jean-Philippe : Lille, Orléans
Guglielmetti Robert: Brest, Marseille, ref. Baillet 1993, Samat 2001, C n, E g
Guillard Chantal : Lyon, ref. 2005, Cermenati 1997, Houas 2001, Danion 2004
Guillemin François : Nancy, ref. Frochot 2007, Viriot 2008
Hadziioannou Georges : Bordeaux, Stalmach 2000, Renaud, 2012

Hamelin Olivier : Grenoble, ref. 2011
Heitz Valérie : Strasbourg
Hénin Françoise: Reims, ref. Pete 1986
Herrmann Jean-Marie: Lyon, ref. 1986
Hickson Kevin: Bordeaux
Hirsch Lionel : Bordeaux, ref. Thakur 2011.
Hoffmann Norbert : Reims, ref. 2006
Jacques Patrice : Mulhouse, ref. 1994
Jacquignon Pierre : Perpignan
Jacquot Pierre : Lille
Jardon Pierre : Grenoble, ref. Bonnier 1972, Petrier 1982, Dumas 2004
Jonusauskas Gediminas: Bordeaux Physics, ref, Dumon 1994, Desvergne 2001, Rullière 2005, Leydet 2007
Joussot-Dubien Jacques : I, Bordeaux, ref. 1964, 2009, Lesclaux 1964, Lesclaux 1966, Lamotte 1974, Lamotte 1984, Schuster 1984, Ab, c, Ce, Eb,d, k
Julliard Michel : Marseille, ref. Ea
Kastler Alfred: Bordeaux, Physics
Kawai Stephen : Strasbourg, ref. Gilat 1993
Keller Nicolas: Strasbourg, ref. 2004
Keller-Spitzer Valérie: Strasbourg, ref. Keller 2004
Kern Jean-Marc : Strasbourg
Klymchenko Andrey S.: Strasbourg, ref. Reisch 2014
Kottis Philemon: Bordeaux Physics, ref Dupuy 1978
Lablache-Combier Alain : Lille, ref. 1973, Marko 1983, Couture 1984, Coqueret 1990, A a
Lacombe Sylvie : Pau, ref. 2009, Blanc 2010, Kartheuser, 2012, Eq
Lacoste Jacques: Clermont-Ferrand, ref. 2015
Lafitte Elisabeth: Bordeaux Physics
Lalande Robert: Bordeaux, ref. Calas & Lalande, 1959
Lalevée Jacques : Mulhouse, ref. 2014, Xiao 2015
Lamotte Michel : Bordeaux, ref. 1974, 1984, Ce
Lapouyade René : Bordeaux, ref. Fornier de Violet 1978, Maus 1999, Bouas-Laurent 2000 and 2001, Malaval 2001, B a
Larrieu Kathy : Pau
Lattes Armand: Toulouse, ref. 1982, Rico 1978
Lavielle Lisette : Mulhouse
Lazare Sylvain : Bordeaux, ref. 1989, Ba, Cg
Leclerc Nicolas : Strasbourg

Le Flem Gilles : Bordeaux
Lehn Jean-Marie : Strasbourg, ref. 1977, 1978, 1990, 1995, Kirch 1979, Gilat 1993, Fernández-Acebes 1998, Teulade-Fichou 2001, Ef
Lemaire Jacques : Clermont-Ferrand, Nancy, ref. 1982, André 1971, Aa
Lepoutre Gérard : Lille, ref. Debacker 1983
Lerner David : Montpellier, ref. 1982
Lesclaux Robert : Bordeaux, ref. 1964, 1966, Joussot-Dubien 1964, Veyret 1989, Caralp 1999, Raoult 2004, Ad, Ba
Létard Jean-François : Bordeaux, ref. 1997
Levisalles Jacques : I, Nancy, Aa
Liotard Daniel: Bordeaux, Pau
Lhomme Jean : Grenoble, ref. Le Doan 1987
Lochet Robert: Bordeaux Physics, ref. Cadas 1962
Loiseau Frédérique : Grenoble, ref. Liatard 2013, Hamelin 2011
Loison Jean-Christophe: Bordeaux
Lokshin Vladimir : Marseille, ref. Samat 2001
Loucheux Claude : Lille, ref. Coqueret 1990
Lougnot Daniel-Joseph: Mulhouse, ref. Fouassier 1987, Saimov 2003
Lounis Brahim: Bordeaux Physics
Loustauneau Pierre: Bordeaux Physics, ref. 1963
Mahiou Rachid : Clermont-Ferrand, ref. Boyer 2012, Adumeau 2015
Mailhot Bénédicte : Clermont-Ferrand
Mailhot Gilles : Clermont-Ferrand, ref. Delort 2015
Malrieu Jean-Paul : Toulouse, ref. 1984, Daudel 1967, Huron 1973, Oliveros 1979, Aa
Mani Jean-Claude : Montpellier
Marko Jean : Lille, ref. 1983
Marteel Jean-Pierre : Lille
Massoulier André: Bordeaux Physics
Mathonière Corine : Bordeaux, ref. Bleuzen 2009, Zhang 2014
Maurette Marie-Thérèse : Pau, Toulouse, ref. Monneyron 2003, Cantau 2006, Ci,
McClenaghan Nathan : Bordeaux, ref. Huang 2005, Leydet 2007, Tron 2015a and 2015b, E c
Méallier Pierre : Lyon
Mégel Jacques: Bordeaux Physics
Mély Yves : Strasbourg, ref. Reisch 2014, Ghose 2015

Ménage Stéphane : Grenoble, ref. Hamelin 2011
Merle Anne-Marie : Bordeaux, ref. Lamotte 1974
Merlin André : Nancy, Ba
Meybeck Jean : Mulhouse
Metzger Jacques : Marseille
Micheau Jean-Claude : Cachan ENS, Toulouse, ref. Delbaere 2002, Berthet 2006
Mignonac Georges : Toulouse
Millié Philippe : Orsay CEA, ref. Bouvier 2003
Moine Bernard : Lyon, ref. 2006.
Monari Antonio : Lyon, Nancy, ref. Dumont 2015
Mordon Serge : I, Lille ESP, Frochot 2015
Morlat-Thérias Sandrine : Clermont-Ferrand, ref. Lacoste 2015
Morlet-Savary Fabrice : Mulhouse, ref. Lalevée 2014, Xiao 2015
Mortier Michel : Paris ENSCP, Grenoble, ref. Cordier 2015
Mousseron-Canet Magdeleine : Montpellier, ref. 1964, Aa, Ca
Moustrou Corinne : Marseille
Moutet Jean-Claude : Grenoble, ref. 1982, Cosnier 1985
Muel Bernard : Orsay Institut Curie, Bordeaux, ref. Kulucsics 1999
Muzart Jacques : Reims, ref. 1980, Pete 1986
Naulin Christian : Bordeaux, ref. Dorthe 1985, Cheldeville 2013, Bergeat 2015
Nakhimovsky: Bordeaux, Ce
Nardello Véronique : Lille, ref. 1996, Ruyffelaere 2013
Niclause Michel : Nancy, ref. André 1971, Aa
Nicoud Jean-François : Strasbourg, ref. Zyss 1984
Nierengarten Jean-François : Strasbourg, ref. Figueira-Duarte 2006, Armaroli 2006, Barrejón 2014
Nouchi Guy: Bordeaux Physics, ref Loustauneau 1963, Dorthe 1985
Oliveros Esther : Pau, Toulouse, ref. 1979, Lattes 1982, Legrini 1993, Monneyron 2003, Pignatello 2006, Lacombe 2009, Ronzani 2013, Ci, Dc
Ollivier Jean : Pau
Orgin Emmanuele : Strasbourg, ref. 2014
Orrit Michel: Bordeaux, Physics, ref 1990, Gaiduk 1999
Paillous Nicole : Toulouse, ref. Gicquel 2000, Gélis 2003
Pale Patrick : Reims
Pénigault Edouard : Mulhouse, ref. Sandorfy 1986

Pete Jean-Pierre : I, Paris ESPCI, Reims, ref. 1986, 1996, Deshayes 1975, Muzard 1980, Migirdicyan 1981, Belotti 1985, Portella 1985, cf Les Associations Européenes, ESCPI.
Pfister-Guillouzo Geneviève : Pau
Pichat Pierre : Lyon, ref. 2003, 2010, 2013, 2014, Ba, Dg, Serpone 1995.
Pigot Thierry : Pau
Piva Olivier : Lyon, Reims, ref. Pete 1986
Poizat Olivier : Lille, ref. De Waele 1999, Sliwa 2010, Stoll 2014
Poquet Elisabeth : I, Pau, ref. Cardy 1981 et 1985, Aa,b
Portella Charles : Reims, ref. 1985, Deshayes 1975, Belotti 1985
Pouyet Bernard : Lyon, ref. Percherancier 1995, Aa
Pouchan Claude : Pau
Poulicard Jacques : Pau
Pozzo Jean-Luc : Bordeaux, ref. Ahmed 2002, Szalóki 2014, E h
Ravanat Jean-Luc : Grenoble, Markovitsi 2007
Reverdy Gilbert : Grenoble, ref. Cauquis 1967, Moutet 1982
Rayez Jean-Claude : Bordeaux, ref. Veyret 1989, Raoult 2004
Rayez Marie-Thérèse : Bordeaux, ref. Veyret 1989, Raoult 2004
Richard Claire : Clermont-Ferrand, ref. Boule 1999, Ronzani 2013
Rico Isabelle: Toulouse, ref. 1978
Rivaton Agnès : Clermont-Ferrand, ref. Chambon 2008
Rivière Monique : Toulouse, ref. Oliveros 1979, Lattes 1982, Rico 1978
Robert Didier : Lyon, Metz, ref. Bb
Rouch Jacques: Bordeaux Physics
Rousset Auguste: Bordeaux, Physics, ref Cadas 1962, Loustauneau 1963
Rullière Claude: Bordeaux Physics, ref 2005, Lapouyade 1992, Dumon 1994, Desvergne 2001, Leydet 2007
Salem Lionel : Orsay, Bordeaux, ref. 1973, 1974, 1977, Dauben 1975, A a
Salmon Lionel : Toulouse
Salvin Roger : Mulhouse
Samat André : Marseille, ref. 2011
Samori Paolo: Strasbourg, ref. Orgin 2014, El Gemayel 2015
Sarakha Mohamed : I, Clermont-Ferrand, ref. Ronzani 2013
Sauvage François-Xavier : Lille, ref. Debacker 1983
Sauvage Jean-Pierre : Strasbourg, ref. 1994, 1998, Lehn 1977, Collin 2001, Dietrich-Buchecker 2001

Schultz Jean : Mulhouse
Servant Yves: Bordeaux Physics
Seta Patrick : Montpellier, ref. 1985
Shafizadeh Niloufar : Saclay CEA
Slaoui Abdelilah : Strasbourg, ref. Collins 2007
Sliwa Michel : Lille, ref. 2010, Stoll 2014, Mély 2015
Soppera Olivier : Mulhouse
Stauffer Louise : Mulhouse
Streith Jacques : Mulhouse, ref. 1966, 1977.
Tanielian Charles : Strasbourg, ref. 1996, 2000, 2003, Schmidt 1994
Thérias Sandrine : Clermont-Ferrand, ref. Lacoste 2015
Toupance Thierry : Bordeaux, ref. Uddin 2012
Trommsdorff Hans-Peter: Orsay, Grenoble, ref. 1995, Vockler 1977, Ern 2001
Turlet Jean-Marie: Bordeaux Physics
Valentin François: Bordeaux Physics

Toward Rules to Understand Photoinduced Dynamics in Organic Molecules

Oliver Schalk
Department of Physics, Stockholm University, 106 91 Stockholm, Sweden

Investigations of photoinduced dynamics of organic molecules have a long history and many different experimental and theoretical tools have been developed to disentangle the myriad of pathways a molecule can take upon light excitation. Despite these efforts, many questions regarding reaction mechanisms and product yields are still unresolved. In order to make progress, it is of fundamental importance to develop a set of rules that can predict the outcome of photochemical processes.[1] Those rules should not only shape our general understanding of how light-induced reactions work but also to help developing functional materials that base on light absorption by tailoring existing ones in order to enhance the desired photochemical outcome. In this contribution, we present out bottom-up type approach toward such rules and show first results.

The outline of this approach is straightforward: Start with simple molecules, i.e. small, unsaturated hydrocarbons/polyenes, then add isolated functionalities to understand their influence on the hydrocarbon, and finally increase the complexity and the size of the systems. As experimental method, we typically use time-resolved photoelectron spectroscopy and compare our findings with those from ab initio calculations.

Our results on hydrocarbons showed that the molecules exhibit a tendency to localize their dynamics at a confined region which we called "dynamophore"[2, 3] as opposed to the chromophore which is typically the more extended part of the molecule where light is absorbed. In contrast to chromophores, there exists only a limited number of dynamophores, the most important one being the ethylene dynamophore which we discuss in some more detail in the following. Other dynamophores are the allyl subunit (CH_2-CH=CH) which gives rise to a [1,3] hydrogen

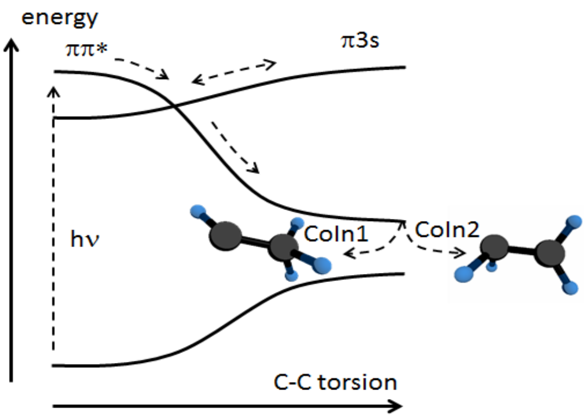


Figure 1. Sketch of the dynamics of ethylene upon excitation to its lowest lying ππ*-state.

shift[2] or the cyclohexa-1,3-diene dynamophore which shows a ring opening reaction.[4]

The dynamics of ethylene are summarized in Figure 1. Upon excitation to its lowest lying ππ* state, a twist about the C-C bond pushes the wavepacket toward two distinct conical intersections (CoIns) with the ground state, one which exhibits a [1,2] H-migration (CoIn1) while the other shows pyramidalization at one carbon atom (CoIn2). This causes a “sudden polarization” of the molecule because the pyramidalized carbon atom is better at stabilizing a negative charge.[5] These dynamics take place on a sub 50-fs timescale and characterize the ethylene dynamophore. In addition, it was observed that, along the torsion coordinate, the ππ* state intersects with a π3s Rydberg state which can be transiently populated before the wavepacket proceeds to the CoIns.[5,6]

Once the dynamics of a dynamophore is understood, the important question is how it manifests in a given molecule. In cyclic polyenes, three main possibilities exist: In the planar cyclopenta-1,3-diene, the dominant relaxation channel is a ring puckering mode at one of the two double

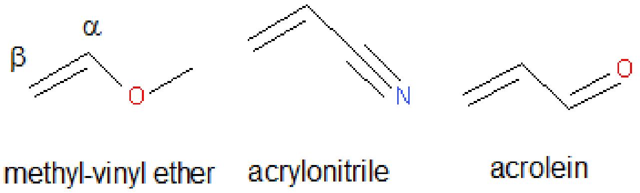


Figure 2. Sketch of the substitutes ethylene molecules

bonds (while the other double bond mainly acts as a "spectator"). This means that one of the carbon atoms „puckers" out of the plane and the neighboring hydrogen twist by almost 90 degrees such that the carbon atom is pyramidalized.[1,7] This puckering dynamics is observed in various small ring molecules such as furan[8] and pyrrole.[9]

In cyclohexene and cyclohexa-1,4-diene, the α-C-C bond next to the double bond can break in order for the molecule to pyramidalize a carbon atom.[2] In the same molecules, the third possibility, namely [1,2] hydrogen migration, is also accessible.

In open chained molecules, localization at the ethylene dynamophore often leads to cis-trans isomerization or pyramidalization at one carbon site. However, less work has been done on this type of molecules.

In the next step, we asked how the ethylene dynamics is modified when replacing one hydrogen atom by a functional group. Studies were performed on methoxy-ethylene[10] (aka methylvinyl ether, see Figure 2), cyanoethylene[11] (aka acrylonitrile), and ethylene-aldehyde[12] (aka acrolein). Upon excitation to the lowest lying bright $\pi\pi^*$ state, all three molecules exhibit typical ethylene-type dynamics that occur within 100 fs for methylvinyl ether and acrylonitrile. Further details became evident when replacing one extra hydrogen atom of the ethylene group by a methyl group in either α- or β-position (see Figure 2) in order to increase the inertia. In a pure dynamical picture, one would assume that substitution in β-position would decelerate the dynamics more because rotation and pyramidalization are both slowed down; however, the opposite turned out to be true. For example in acrylonitrile, the CN-group creates a negative charge at the α–carbon atom enforcing pyramidalization in α–position. If the molecule is substituted in this position, the dynamics is slowed down[11] leading to lower internal conversion rates in a Landau-Zener type picture (i.e. the probability for internal conversion decreases for a lower momentum of the wavepacket). Similar results were found for acrolein.[12]

Currently, we are systematically studying five-membered heterocycles including nitrogen, oxygen and sulfur atoms. First results show that the interplay between ring puckering, C-O bond cleavage and N-H bond fission is crucial. For example in furan, the interplay between the ring puckering and the ring opening channel is not yet resolved.[8] Therefore, the aim is to find rules to rationalize under which conditions the different channels are accessed.

Other important issues when developing rules for light induced processes in organic molecules are (i) the different reaction pathways that can be taken upon excitation to different electronic states either by different excitation energies or different number of photons (see reference 13 for an example on 1,3-butadiene) and (ii) the changes induced by excited states that can be transiently populated in the course of the dynamics. One topic that was under-appreciated in the past but might turn out to be crucial is the role of Rydberg states. In methyl-vinyl ether, for example, excitation of the $\pi\pi^*$ state leads to fast, ethylene-type dynamics.[4] However, when exciting the close lying Rydberg state, the wavepacket can progress either via the $\pi\pi^*$ or a $\pi\sigma^*$ state. The latter leads to ultrafast bond cleavage of the C-O group forming a methoxy and a vinyl radical. More subtle are the cases where Rydberg states are intermediate states after valence state excitation as shown in Figure 1 for ethylene.[5,6] These cases are hard to address by ab initio computations but the effects on the outcome of the reaction might be as drastic as shown for the vinyl ethers upon direct access of the Rydberg state.[4] We recently discovered such a behavior in pyrrole and some methylated derivatives: Upon excitation of the lowest lying bright $\pi\pi^*$ state, we found that a π3pRydberg state is passed in the dynamics pathway.[9] It is possible that this Rydberg state redirects the outcome of the dynamics from N-H fission to a ring puckering intersection with the ground state, hence directly affecting the yield of fast hydrogen atoms. The role of Rydberg states might become more important when people start looking at processes initiated on higher lying excited states. However, it is clear that dynamics are more complex than described by the old notion that the fate of a photoinduced reaction is decided on the lowest lying potential energy surface irrespective of which states were accessed before.

In summary, excited state dynamics of organic molecules are complicated, but certain trends can be observed. We are working on schemes how to understand the driving forces behind these reactions by means of "simple" rules. A first success has been the observation that dynamics tend to localize at "dynamophores" and how the chemical environment of a dynamophore can influence the dynamics.

References.

[1] O. Schalk, A. E. Boguslavskiy, and A. Stolow, *J. Phys. Chem. A*, **114**, 4058-4064 (2010).

[2] O. Schalk, A. E. Boguslavskiy, A. Stolow, M. S. Schuurman, *J. Am. Chem. Soc.* **133**, *16451-16458* (2011).

[3] O. Schalk, A. E. Boguslavskiy, M. S. Schuurman, A. Stolow, *EPJ Web of Conferences* **41**, 02037 (2013)

[4] O. Schalk, M. Stenrup, T. Geng, R. Lindh, R. D. Thomas, R. Feifel, T. Hansson, *J. Phys. Chem A*, **119**, 9225-9235 (2015).

[5] T. Mori, W. J. Glover, M. S. Schuurman, T. J. Martinez, *J. Phys. Chem. A* **116**, 2808-2818 (2012).

[6] E. G. Champenois, N. H. Shivaram, T. W. Wright, C. S. Yang, A. Belkacem, J. P. Cryan, *J. Chem. Phys.* **144**, 014303 (2016).

[7] T. J. A. Wolf, T. S. Kuhlman, O. Schalk, T. J. Martinez , K. B. Møller, A. Stolow, A.-N. Unterreiner, *Phys. Chem. Chem. Phys.* **16**, 11770-11779 (2014).

[8] S. Oesterling, O. Schalk, T. Geng, R. D. Thomas, T. Hansson, R. De Vivie-Riedle (submitted).

[9] T. Geng, O. Schalk, S. P. Neville, T. Hansson, R. D. Thomas (submitted).

[10] O. Schalk, M. Stenrup, T. Geng, R. Lindh, R. D. Thomas, R. Feifel, T. Hansson, *J. Phys. Chem. A* **119**, 11105-11112 (2015).

[11] R. J. MacDonell, O. Schalk, T. Geng, R. D. Thomas, R. Feifel, T. Hansson, M. S. Schuurman, *J. Phys. Chem.* **145**, *114306* (2016).

[12] A: M. D. Lee, J. D. Coe, S. Ullrich, M.-L.; Ho, S.-J. Lee, B.-M. Cheng, M. Z. Zgierski, I.-C. Chen, T.-J. Martinez, A. Stolow, *J. Phys. Chem A* **111**, 11948-11960 (2007).

[13] O. Schalk, A. E. Boguslavskiy, A. Stolow, *Chem. Phys. Lett.* **5**, 560 (2014).

Fluorescence spectroscopy as useful method to predict photodynamic efficacy

Vanya N. Mantareva
Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Fluorescence properties of the compounds studied as photosensitizers (PS) for photodynamic therapy (PDT) are under special consideration during their investigations.[1,2] The molecular time-resolved fluorescence spectroscopy appears a significant tool for evaluation of the compounds capability to act as PDT sensitizers.[3] The time of fluorescence refers to the time when the PS participate in the photosensitization process and the phototoxicity towards the target cells can happen. The origin of the PDT owns to the visible or near infra-red light excitation of PS which converts to its singlet excited state. Thus initiates further physical transition like the fluorescence emission. In case of PS with absorption in visible spectrum and the relatively intensive fluorescence, this can be useful property for imaging and detection of the damage tissues.[4]

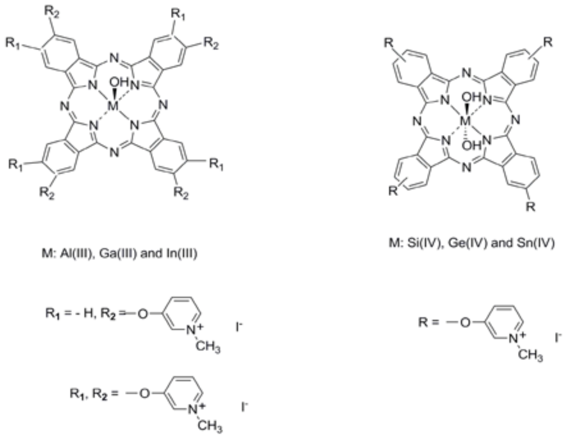


Figure 1. Chemical structure of quaternized metallophthalocyanines with properties suitable for PDT applications.

The medical diagnosis known as optical biopsy is a well-accepted, non-invasive method for detection of an early stage, small and superficial tumours.[5] The method is based on the fluorescence characteristics of the native tissue chromophores such as amino acids, enzymes, proteins but mainly the haemin (the dye molecule which is part of haemoglobin) which possess wide band of the emission in the visible spectrum (Ex/ Em = 540/ 600 nm) with different characteristics for damaged and normal tissues.[4,5] On the other hand the specificity of vascular system also leads to altered oxygenation of haemin and other intracellular chromophores and the fluorescence varies in dependence on the oxidation status of the native chromophores as well as the uptakes of applied exogenous compound.[6]

During the recent years a highly conjugated heterocyclic compounds such as phthalocyanines have been intensively studied as photosensitizers for the PDT applications.[2] The phthalocyanine complexes of Cu(II) and ClAl(III) were firstly discovered by chance in the beginning of last century and nowadays they are among the most applicable dyes and pigments starting from their traditional application to the modern usages in technology and biomedicine. Considering the chemical structure, fluorescence property depends mainly on the substituents attached to the Pc macrocycle or substituents in axial position to the coordinated metal ions. In addition to the structural characteristics of the phthalocyanines the conditions such as the solvents properties, the heterogeneity of the media, temperature and the excitation light source could be varied to have sufficient evaluation of their potential effectiveness as PDT agents.

A fluorescent molecule studied in solution can be used for localization and visualization of the target pathogenic cells. In addition, non-radiative energy transfer to produce the PS in triplet excited state is responsible for the further phenomenon of an energy transfer to the molecular oxygen, which in its ground state is a triplet molecule and in the excited state is a singlet electronic state. Two fluorescence modes namely steady-state and time-resolved fluorescence, both give the opportunity to study the optical properties of compounds. They are designed for harmless and fast photodiagnosis of small and early stage tumours considering the fluorescence of the introduced photoactive compounds which are applying as well as for PDT.

Table 2. Absorption and fluorescence maxima and life-times of fluorescence for quaternized MPcs given in Fig. 1, all measured in dimethylsulphoxide and a standard ZnPc.

Photosensitizer	**Absorption**	**Fluorescence**	**Fluorescence life time**
	λ, nm	**λ, nm**	**τ_f, ns**
ZnPcMe	674	688	3.450
AlPcMe	677	683	4.871
GaPcMe	683	696	4.578
InPcMe	697	716	3.661
SiPcMe	676	680	4.273
GePcMe	681	686	4.071
ZnPc*	671	683	3,999

* ZnPc is used as a standard compound.

The fluorescence properties of the water-soluble different metals phthalocyanine complexes (Fig. 1), all recently studied by us as effective antimicrobial agents *via* PDT, are summarised in our recent review paper.[7] The phthalocyanines as the photosensitizers have light absorption ~ 675 nm and the excitation band at ~ 610 nm is usable for and fluorescence emission with maximum > 680 nm which is red shifted towards the absorption band. The further relaxation process of the absorbed energy is by the non-radiative transition of the molecule in the singlet excited state to the lower energy triplet excited state by the intersystem crossing transition. Most of the studied MPcs for PDT undergo the singlet-singlet radiative transition with detectable fluorescence emission (fluorescence quantum yields of 0.2 – 0.4) and fluorescence life-time with values between 3.45 – 4.87 nm (Table 2).

References.

1. Miheev, G.M., Angelov, I.P., Mantareva, V.N., Mogileva, T.N., Miheev, K. G. Thresholds of Optical Power Limitation in Solutions

of Nanoscale Compounds of Zinc Phthalocyanine with Galactopyranosyl Radicals, *Technical Physics Letters*, *39*(7), 664-668 (2013).

2. Dumoulin, F., Nyokong, T., Ahsen, V. In: *Photosensitizers in Medicine, Environment, and Security*, Springer, Netherlands, pp. 664, (2012).

3. Prasanth, C. S. Karunakaran, S., Paul, V., Kussovski, V., Mantareva, V., Ramaiah, D., Selvaraj, L., Angelov, I., Krishnankutty, N., Avramov, L., Subhash, N. Antimicrobial Photodynamic Efficiency of Novel Cationic Porphyrins towards Periodontal Gram-positive and Gram-negative Pathogenic Bacteria, *Photochem. Photobiol.*, 90 (3), 628-640 (2014).

4. Rueck, A., Hauser, C., Mosch, S., Kalinina, S. Spectrally resolved fluorescence lifetime imaging to investigate cell metabolism in malignant and nonmalignant oral mucosa cells, *J. Biomed. Opt.* 19(9), 96005-9, (2014).

5. Koenig, K., Schneckenburger, H. Laser-induced autofluorescence for medical diagnosis, *J. Fluoresc.*, 4(1), 17-40, (1994).

6. Borisova, E., Mantareva, V., Bliznakova, I., Angelov, I., Avramov, L., Petkova, E. Photodiagnosis and Photodynamic Therapy of Cutaneous Melanoma, In: *Current Management of Malignant Melanoma*, Ming Y. Chao (Ed.), InTech Publisher, Chapter 7, 140-156 (2011).

7. Mantareva, Angelov, I., Wöhrle, D., Borisova, E., Kussovski, V. Metallophthalocyanines for antimicrobial photodynamic therapy: An overview of our experience, *J. Porphyrins Phthalocyanines*, *17*(6-7), 2013, 399-416 (2013).

Novel strategies of femtosecond spectroscopy and Raman imaging for cancer research

*Rafał Kania, Arkadiusz Jarota and Halina Abramczyk**
Lodz University of Technology, Institute of Applied Radiation Chemistry, Laboratory of Laser Molecular Spectroscopy, Wroblewskiego 15, 93-590 Lodz, Poland.

Introduction: Femtosecond spectroscopy combined with Raman imaging may open new expanses in cancer biology particularly in metabolic and epigenomic modifications of cancer, and bring revolution in cancer detection and treatment. High spatial[1-9] and temporal resolution[10-12] allows to detect a single cancerous cell in vivo, monitor molecular events that occur inside and contribute to cancer development.

Phthalocyanines, synthetic cousins of naturally occurring porphyrins, due to their diverse properties including high thermal and optical stability, tunable optical properties, and the tendency to form π-π stacks found broad application such as dyes, optoelectronic devices and photosensitizers in photodynamic of cancer (PDT).[13,14] Ultrafast optical properties of phthalocyanines have been extensively studied in solution[12,15-17] and film[18,19], though there is relatively little research on phthalocyanines adsorbed at biological interfaces. According to our best knowledge no femtosecond dynamics of PDT photosensitizers in human cancerous vs. non-cancerous tissue have been reported yet.[10-13]

Recently, we have studied electronic dynamics of two representative photosensitizers, tetrasulphonated aluminum phthalocyanine ($AlPcS_4$) and tetrasulphonated zinc phthalocyanine ($ZnPcS_4$) in aqueous solution, thin film and in non-cancerous and cancerous human breast tissue.[10,12,20] The $ZnPcS_4$ differs from $AlPcS_4$ in tendency to form co-facial dimers and higher aggregates in aqueous solution.[12,16] In the first section of this paper we discuss results of ultrafast transient absorption measurement for both PDT dyes in aqueous solution.[10,12] Thanks to our cooperation with Lodz Medical University and Copernicus hospital we were able to study photosensitizer stained samples of human tissue that were

---

* Corresponding author: abramczy@mitr.p.lodz.pl

histopathologically evaluated and identified to be tumor affected and tumor-free. The second section is devoted to comparison of electronic relaxation mechanisms of our photosensitizers in solution to tumorous and tumor-free ex-vivo human tissue environment. The last section of this paper gives account of our spatially resolved confocal Raman Imaging (RI) technique studies that explore both differences in photosensitizers concentration distribution in tumorous and tumor-free tissues as well as biochemical properties of the tissues itself.

Experimental: Our laser system based spectrometer used for studying ultrafast transient absorption has been thoroughly described at *Brożek-Płuska B. at all.*[16] while the Raman Imaging measurements were done on Alpha 300RA (WITec) spectrometer system combined with optical microscope (Olympus).

Phthalocyanines in solution: The ultrafast transient absorption (TA) spectroscopy measurements of $AlPcS_4$ derivative in H_2O were conducted for excitation at Q-Band (670 nm) and B-band (330 nm) while system response was collected from bleach of Q-band absorption (670 nm) and the excited state absorption (ESA) at 570 nm. To compare electronic relaxation mechanisms of both phthalocyanines we acquired TA absorption for $ZnPcS_4$ at Q-band frequency. The Fig. 1 displays transient absorption TA decay traces of ESA band for both compounds. Fitting of time decay curves has been done assuming tri-exponential decay dynamics for all traces but ESA band of $AlPcS_4$ were fourth exponential decay has been found. The TA trace fitting data is collated in Table 1. In case of $AlPcS_4$ the TA data we observe consistent picture for Q- and B-band excitation experiments. Observed only for $AlPcS_4$ derivative the fastest component in the range below 1ps was assigned to wavepacket dynamics. The decay component in range of 2-15 ps was assigned to vibrational relaxation processes. Vibrational relaxation process is followed by population decay from the S_1 excited state to a S_0 ground state in timescales of 25-75 ps. The slowest hundred picosecond lifetime observed in solution was assigned to relaxation to the ground state resulting from process of back inter system crossing from triplet state. Comparing data for aluminum and zinc phthalocyanine derivatives indicates slower rates of internal conversion processes for the latter while leaving excited state S_1 depopulation rate intact.

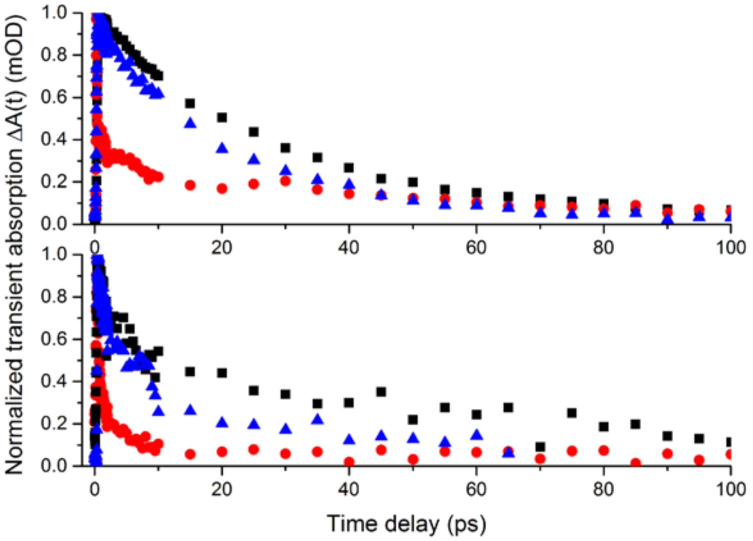


Figure 1. Normalized transient absorption signal decay of ESA band for ZnPcsS$_4$ (top), AlPcS$_4$ (bottom) in aqueous solution (■) and at cancerous (▲) and cancer-free (●) tissue. Signals were recorded for pumping pulse centered at 674 nm while probing at 570 nm. The sample in aqueous solution had concentration around 10^{-3} M.

Phthalocyanines in thin film and at the biological interfaces: To gain inside into ultrafast electronic relaxation mechanism of PDT photosensitizers in therapeutic environment we recorded TA spectra in thin 6-16um thin stained cancerous and cancer-free human tissue resections. Examples of recorded TA signals for both types of tissue and staining agent are shown in Fig. 1 while fitting results are collated in Table 1. Consistently for both phthalocyanine derivatives we observed marked increase of electronic relaxation rates. We observed total disappearance of slowest lifetime observed in solution at above hundred picoseconds in the same time new component appear with lifetimes below 2 ps. The loss of slowest lifetime component is consistent with RI observed quenching of phthalocyanines fluorescence at biological interfaces that can be linked to generation of singlet oxygen $^1O_2$ in the process of triplet-triplet annihilation. The fastest and most prominent electronic relaxation processes for phthalocyanies at biological interfaces are wavepacket dynamics. The wavepacket dynamics and vibrational relaxation processes are markedly faster in tissue environment than in solution. While excited state relaxation to a ground state showing values in similar range to those observed in solution. In order to estimate impact of phthaolcyanine self-aggregation on electronic relaxation rates we performed TA measurements in thin film. Comparison of the thin film with solution and tissue data (Tab. 1) indicates that electronic relaxation processes are the fastest at biological interfaces than in thin film and in solution. We conclude that observed TA decay rate differences are associated with environment specific electronic excitation relaxation channels. Finally, the lifetime characterizing both the ground state S_0 and the first excited state S_1 in the interfacial regions of noncancerous tissue are markedly shorter than those in cancerous tissue making ultrafast TA spectroscopy a diagnostic tool in cancer detection.

Table 1. The fitting results of ultrafast transient absorption decay traces for $ZnPcS_4$ and $AlPcS_4$ recorded in solution, thin film and tumor-free and tumorous human tissue.

$ZnPcS_4$	Wavelength [nm]		Lifetime [ps]			
	Pump	Probe	τ_1	τ_2	τ_3	τ_4
Aqueous solution	674	674	-	11.1 ± 0.9	25.9 ± 0.5	307±79
	633	633	-	12.1 ± 0.7	73 ± 14	116±27
	674	570	1.3 ± 0.3	-	21.6 ± 1.2	108±16
film	674	674	1.8 ± 0.2	13.1 ± 0.8	28.4 ± 1.8	-
	674	570	1.3 ± 0.1	11.7 ± 1.5	49.2 ± 2.5	-
Tumor-free tissue	674	674	1.7 ± 0.4	24.4 ± 3.1	59.3 ± 4.4	-
	674	570	1.0 ± 0.1	1.6 ± 0.2	8.9 ± 0.2	-
Tumor tissue	674	674	8.3 ± 1.2	17.8 ± 1.7	42.2 ± 1.6	-
	674	570	2.7 ± 0.2	11.6 ± 0.5	37.0 ± 0.6	-
$AlPcS_4$						
Aqueous solution	677	670	-	4.3 ± 1.7	47 ± 124	232±81
	678	570	0.50±0.09	2.4 ± 0.7	28 ± 24	345±108
film	677	670	0.8 ± 0.1	7.3 ± 0.1	56.0 ± 6.6	-
	677	602	0.16±0.03	1.5 ± 0.4	21.6 ± 4.1	-
Tumor-free tissue	677	670	0.1 ± 0.01	1.3 ± 0.2	40.7 ± 7.9	-
	677	602	0.18±0.02	0.8 ± 0.4	6.0 ± 1.9	-
Tumor tissue	678	660	0.1 ± 0.01	1.5 ± 0.2	37.8 ± 5.3	-
	677	602	0.8 ± 0.04	5.6 ± 5.5	60 ± 13	-

Spatial distribution of phthalocyanines at biological interfaces a Raman Imaging study: Our RI investigations started by analyzing composition of the healthy and tumor affected breast tissue.[21] Pathology of cancer development in breast tissue is related to uncontrolled growth of epithelial cells lining milk ducts. In carcinogenesis rapidly multiplying epithelial cells displace surrounding breast adipose cells. Hence we concentrate our effort at adipose cells components fingerprint in Raman spectrum to find indications of tumor cells development. An example of such RI study of tissue from is shown in Fig. 2.

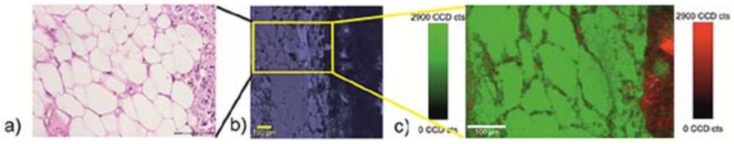


Figure 2. The breast tissue from the margin of the tumor mass (dark/red areas): H&E-stained histological image (a), microscopy image (b), Raman image (c).[6]

We found changes in Raman spectrum indicative of tumor presence that may be used as biomarker of cancer tissue presence. This discovery combined with miniaturization and automation of Raman spectrometers gives a promise of constructing a Raman probe system for a mid-operation detection of cancerous tissue. We continued our RI investigation by using samples stained with investigated photosensitizers.[6,10] The Raman microscopy image revealed sharp division of photosensitizer concentration between cancerous and noncancerous regions. The tumor free regions show generally low aggregation of photosensitizer mainly on the outer cell membrane. On the other hand the cancerous tissue was showing stronger and uniform distribution of photosensitizer within cell mass. The results presented here demonstrate that Raman spectra images are sensitive indicators of distribution of different compounds in tissue both natural and xenobiotic and they have diagnostic value equivalent to histopathological investigations.

Conclusions: In summary the Raman imaging can unravel morphology, biochemistry and photochemistry of human tissue that benefit cancer research. The spatially resolved Raman spectroscopy can monitor epigenetic processes such as acetylation/methylation processes in cells a hallmark of carcinogenesis. The combined Raman/fluorescence imaging exhibits great potential for photodynamic therapy monitoring the distribution of photosensitizers and the biochemical distribution of tissue components. Finally, the changes in femtosecond dynamics of the photosensitizer can be employed as an important indicator of the cancer pathology.

Future perspectives: A successful treatment of tissue samples with ultrafast TA has inspired us to employ mid-infrared based techniques to study electronic relaxation of phthalocyanine based dyes using time-resolved infrared spectroscopy. The fact that mid-infrared light does not induce photochemical processes suggests go for all mid-infrared techniques such as two-dimensional infrared spectroscopy[22] to study both cells constitution and probe environment around dye molecules.

The application of ultrafast pulses in mid-IR spectral region paves a way for understanding mechanistic aspects of important photochemical reactions including excited-state proton transfer between DNA strands [23], ring opening in 7-dehydrocholesterol that constitutes the first step of Vitamin D_3 formation [24,25] or ring opening/closure reaction in diarylethenes, a family of photochromic switches [26]. The latter mentioned group of compounds due to high thermal and optical stability and high fatigue resistance found versatile applications - from molecular electronics [27] to super-resolution imaging[28], biological markers[29], and bioactivity controls[30]. The employment of time-resolved experiments in mid-IR will facilitate to unravel key nuclear motions involved in ring/opening reactions in diarylethene derivatives, the information that is usually blurred by electronic dynamics in time-resolved experiments in UV-VIS spectral region [31,32]. The elucidation of ultrafast vibrational dynamics will provide a feedback for chemists involved in design of compounds with desired optical properties.

Acknowledgments: The project was funded through The National Science Centre Poland Grants UMO-2015/19/B/ST4/01878 and UMO-2015/19/D/ST4/01813.

References:

1. Abramczyk, H. *et al.* Epigenetic changes in cancer by Raman imaging, fluorescence imaging, AFM and scanning near-field optical microscopy (SNOM). Acetylation in normal and human cancer breast cells MCF10A, MCF7 and MDA-MB-231. *Analyst* **141**, 5646-5658 (2016).
2. Abramczyk, H. & Brozek-Pluska, B. New look inside human breast ducts with Raman imaging. Raman candidates as diagnostic markers for breast cancer prognosis: Mammaglobin, palmitic acid and sphingomyelin. *Analytica Chimica Acta* **909**, 91-100 (2016).
3. Abramczyk, H. *et al.* The role of lipid droplets and adipocytes in cancer. Raman imaging of cell cultures: MCF10A, MCF7, and MDA-MB-231 compared to adipocytes in cancerous human breast tissue. *Analyst* **140**, 2224-2235 (2015).
4. Surmacki, J., Brozek-Pluska, B., Kordek, R. & Abramczyk, H. The lipid-reactive oxygen species phenotype of breast cancer. Raman spectroscopy and mapping, PCA and PLSDA for invasive ductal carcinoma and invasive lobular carcinoma. Molecular tumorigenic mechanisms beyond Warburg effect. *Analyst* **140**, 2121-2133 (2015).
5. Brozek-Pluska, B., Kopec, M., Niedzwiecka, I. & Morawiec-Sztandera, A. Label-free determination of lipid composition and secondary protein structure of human salivary noncancerous and cancerous tissues by Raman microspectroscopy. *Analyst* **140**, 2107-2113 (2015).
6. Abramczyk, H., Brozek-Pluska, B., Surmacki, J., Musial, J. & Kordek, R. Oncologic photodynamic diagnosis and therapy: confocal Raman/fluorescence imaging of metal phthalocyanines in human breast cancer tissue in vitro. *Analyst* **139**, 5547-5559 (2014).
7. Abramczyk, H., Brozek-Pluska, B., Krzesniak, M., Kopec, M. & Morawiec-Sztandera, A. The cellular environment of cancerous human tissue. Interfacial and dangling water as a "hydration fingerprint". *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **129**, 609-623 (2014).
8. Abramczyk, H. & Brozek-Pluska, B. Raman imaging in biochemical and biomedical applications. Diagnosis and treatment of breast cancer. *Chemical Reviews* **113**, 5766-5781 (2013).

9. Surmacki, J., Musial, J., Kordek, R. & Abramczyk, H. Raman imaging at biological interfaces: Applications in breast cancer diagnosis. *Molecular Cancer* **12** (2013).
10. Abramczyk, H., Brozek-Pluska, B., Surmacki, J., Tondusson, M. & Freysz, E. Photostability of biological systems—Femtosecond dynamics of zinc tetrasulfonated phthalocyanine at cancerous and noncancerous human Breast tissues. *Journal of Photochemistry and Photobiology A: Chemistry* **332**, 10-24 (2017).
11. Abramczyk, H., Brozek-Pluska, B., Tondusson, M. & Freysz, E. Ultrafast dynamics of metal complexes of tetrasulfonated phthalocyanines at biological interfaces: Comparison between photochemistry in solutions, films, and noncancerous and cancerous human breast tissues. *Journal of Physical Chemistry C* **117**, 4999-5013 (2013).
12. Jarota, A., Tondusson, M., Galle, G., Freysz, E. & Abramczyk, H. Ultrafast Dynamics of Metal Complexes of Tetrasulphonated Phthalocyanines. *The Journal of Physical Chemistry A* **116**, 4000-4009 (2012).
13. Brozek-Pluska, B., Orlikowski, M. & Abramczyk, H. in *Handbook of Porphyrin Science* Vol. Volume 39 *Handbook of Porphyrin Science* 1-49 (World Scientific Publishing Company, 2016).
14. The Phthalocyanines, I., II, Moser, F. H. & Thomas, A. L. *FL.* (1983).
15. Brożek-Płuska, B., Czajkowski, W., Kurczewska, M. & Abramczyk, H. *J. Mol. Liq.* **141**, 140 (2008).
16. Brożek-Płuska, B., Jarota, A., Kurczewski, K. & Abramczyk, H. *J. Mol. Struct.* **924–926**, 338 (2009).
17. Howe, L. & Zhang, J. Z. Ultrafast Studies of Excited-State Dynamics of Phthalocyanine and Zinc Phthalocyanine Tetrasulfonate in Solution. *The Journal of Physical Chemistry A* **101**, 3207-3213 (1997).
18. Ma, Y.-Z., Xiao, K. & Shaw, R. W. Exciton–Exciton Annihilation in Copper-phthalocyanine Single-Crystal Nanowires. *The Journal of Physical Chemistry C* **116**, 21588-21593 (2012).
19. Terasaki, A. *et al. J. Phys. Chem.* **96**, 10534 (1992).
20. Abramczyk, H., Brozek-Pluska, B., Tondusson, M. & Freysz, E. Ultrafast Dynamics of Metal Complexes of Tetrasulfonated Phthalocyanines at Biological Interfaces: Comparison between Photochemistry in Solutions, Films, and Noncancerous and Cancerous Human Breast Tissues. *The Journal of Physical Chemistry C* **117**, 4999-5013 (2013).

21. Brozek-Pluska, B. *et al.* Distribution of Phthalocyanines and Raman Reporters in Human Cancerous and Noncancerous Breast Tissue as Studied by Raman Imaging. *Technology in Cancer Research & Treatment* **11**, 317-331 (2012).

22. Hunt, N. T. 2D-IR spectroscopy: ultrafast insights into biomolecule structure and function. *Chemical Society Reviews* **38**, 1837-1848 (2009).

23. Zhang, Y., de La Harpe, K., Beckstead, A. A., Improta, R. & Kohler, B. UV-Induced Proton Transfer between DNA Strands. *Journal of the American Chemical Society* **137**, 7059-7062 (2015).

24. Arruda, B. C., Peng, J., Smith, B., Spears, K. G. & Sension, R. J. Photochemical Ring-Opening and Ground State Relaxation in α-Terpinene with Comparison to Provitamin D3. *The Journal of Physical Chemistry B* **117**, 4696-4704 (2013).

25. Kobayashi, T., Jarota, A. & Xue, B. Laser Original : Application of Ultrashort DUV Pulse Laser to Study the Primary Dynamic Process of Molecules in Vitamin D Biosynthesis (「バイオ分野における紫外・深紫外光の新たな応用展開」特集号). *レーザー研究 = The review of laser engineering : レーザー学会誌* **43**, 703-706 (2015).

26. Kobatake, S., Takami, S., Muto, H., Ishikawa, T. & Irie, M. Rapid and reversible shape changes of molecular crystals on photoirradiation. *Nature* **446**, 778-781 (2007).

27. Irie, M., Fukaminato, T., Matsuda, K. & Kobatake, S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chemical Reviews* **114**, 12174-12277 (2014).

28. Fernandez-Suarez, M. Redirecting lipoic acid ligase for cell surface protein labeling with small-molecule probes. *Nature Biotech.* **25**, 1483-1487 (2007).

29. Roubinet, B. *et al.* Carboxylated Photoswitchable Diarylethenes for Biolabeling and Super-Resolution RESOLFT Microscopy. *Angewandte Chemie International Edition* **55**, 1-6 (2016).

30. Babii, O. *et al.* Controlling Biological Activity with Light: Diarylethene-Containing Cyclic Peptidomimetics. *Angewandte Chemie International Edition* **53**, 3392-3395 (2014).

31. Jean-Ruel, H. *et al.* Femtosecond Dynamics of the Ring Closing Process of Diarylethene: A Case Study of Electrocyclic Reactions in Photochromic Single Crystals. *The Journal of Physical Chemistry A* **115**, 13158-13168 (2011).

32. Ishibashi, Y. *et al.* Solvent Polarity Dependence of Photochromic Reactions of a Diarylethene Derivative As Revealed by Steady-State and Transient Spectroscopies. *The Journal of Physical Chemistry C* **120**, 1170-1177 (2016).

Not All Atoms That Wander Are Lost: Femtochemistry of Halocarbons in the Gas and Liquid Phases

Alexander N. Tarnovsky
Department of Chemistry and the Center for Photochemical Sciences, Bowling Green State University, 43403 Ohio, USA

The last decade has witnessed an explosive growth of our understanding of ultrafast photophysical and photochemical dynamics in various environments. With constantly improving experimental methods, a wealth of detailed insights into the fundamental processes has been obtained. New, unforeseen twists of old tales have emerged. Consider breaking and making of chemical bonds. These two processes lie at the heart of chemistry, can be light-driven, and have been of great interest to scientists. Photodissociation turned out to be a multifaceted process, one facet of which is non-adiabatic dynamics through the potential-energy curve crossing such as a conical intersection.[1,2] A conical intersection accessible from the Franck–Condon point determines the timescale for population decay from the excited electronic state and the molecular fate, that is the occurrence of a specific photophysical or a photochemical pathway. Another twist is unconventional, "roaming" mechanism recently discovered in unimolecular gas-phase dissociation reactions.[3] In roaming, a radical fragment formed as a result of 'frustrated' dissociation of a closed shell molecule "wanders" into a reactive site of the second radical fragment to form molecular products via intramolecular abstraction. The first example of this behavior was observed in the dissociation of formaldehyde where the hydrogen of the significantly stretched –CH bond encounters the other hydrogen and abstracts it, yielding H_2 and CO.[4] Further evidence for roaming reactions was reported in the dissociation of nitromethane and nitrobenzene, and in the photodissociation of acetaldehyde and nitrate radical. Roaming dynamics is non-ergodic, incompatible with statistical theories like classical Transition State Theory, competes with conventional reaction channels for product yields, and leads to new, unexpected reaction outcomes.[3]

The UV photodissociation reactions of a large and (photo)synthetically viable class of naturally occurring and man-made di- and polyhalogenated alkanes are ubiquitous sources of reactive halogens that have impact on atmospheric and environmental chemistry.[5,6] Elucidating the elementary steps at the atomic/molecular level has been of much interest. In our previous work, we made significant progress capturing the electronic spectra of halomethyl radicals and isomers (*iso-*) of di- and polyhalogenated alkanes.[7-11] The isomers, which have weak intramolecular bonds between the halogen atoms, e.g. $CF_2I{-}I$, $CH_2Br{-}Br$, are the key intermediates in a large number of condensed-phase photochemical reactions involving halocarbons. Since 2009, we have been advancing the state-of-the-art technical capabilities for collecting ultrafast transient absorption spectra in the deep-UV to UV range, 200-400 nm, using pulses from optical parametric amplifiers. Because many small radical and ion products only absorb in this spectral region, this is a very important extension of the pump/dispersed-probe technique to photodissociation problems. By utilizing broadly tunable deep-UV-to-UV probe pulses and high time resolution, we have detected transient absorption bands of $CH_2Br\cdot$ at 235 nm, $CH_3CN\cdot Br$ charge-transfer complexes at 272 nm,[10] and I^- at 221 nm,[7] and demonstrated how the controversies in UV photodissociation of $CHBr_3$[11] and CHI_3[7] could be resolved. These observations opened ways to future studies, notably that of $CHBr_3$,[12] requiring clearly defined spectral signatures of reaction intermediates.

In our work on the UV photochemistry of CF_2I_2,[8,13] a new paradigm has come to fore that the reaction coordinate for a C-I bond cleavage is multidimensional. Other normal modes are involved in this photochemical path; $\angle C{-}I$ bending is the most important. We observed the $CF_2I{-}I$ product following 350-nm excitation of CF_2I_2 in CCl_4 (298 K): a 400-fs delayed rise of $CF_2I{-}I$ was observed by probing the C−F stretching mode by ultrafast time -resolved IR.[8] The formation of this isomer in room temperature solutions has direct dynamic implications for the ultrafast production of molecular iodine from CF_2I_2 excited with UV light. $CF_2I{-}I$ has a built-in intramolecular decay channel where the C−F stretch couples to the reactive C−I stretch, leading to I_2 on a 1-ps time scale.[14] The subsequent matrix isolation and computational work on the UV photochemistry of CF_2Br_2 showed that *iso*-CF_2Br_2 is an intermediate in the reaction: $CF_2Br\cdot + Br\cdot = CF_2 + Br_2$.[15] Yet, in these experiments the migrating halogen atom is trapped by a solvent cage. To link this mechanism to molecular halogen photoelimination in halons and freons, such photochemical isomerization needs to be observed in the gas phase, where formation of such molecular products is of major importance to atmospheric photochemistry.[6]

This isomerization path has been observed in the UV photochemistry of bromoform, the largest organic source of bromine to the atmosphere. First, upon UV excitation of $CHBr_3$ in the liquid phase,[11] we have observed geminate recombination (5-10 ps) of $Br\cdot$ and $CHBr_2\cdot$ products into *iso*-$CHBr_3$, Fig. 1. Such cage-induced isomerization mechanisms are frequently invoked in halocarbon literature, but, in fact, this study is the first where this mechanism is directly observed. Further, the work has showed the existence of another, previously unsuspected, isomerization pathway - direct, concerted isomerization of electronically excited $CHBr_3$ through a conical intersection (CI in Fig. 1). This intersection is located between the lowest excited $\tilde{A}\ ^1A_2$ state of $CHBr_3$ and the ground state of *iso*-$CHBr_3$, and in the vicinity of a saddle point on the ground state, which connects the isomer forms;[11] a large fraction of the excited $CHBr_3$ molecules accesses this CI, leading to the 100-fs formation of *iso*-$CHBr_3$ product species.

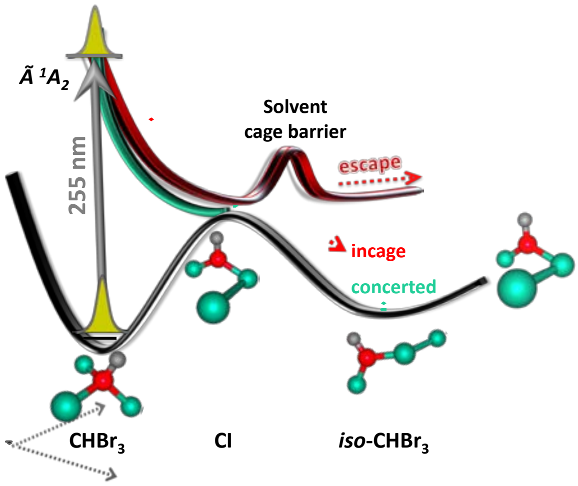


Figure 1. The 255-nm photochemistry of $CHBr_3$.[11]

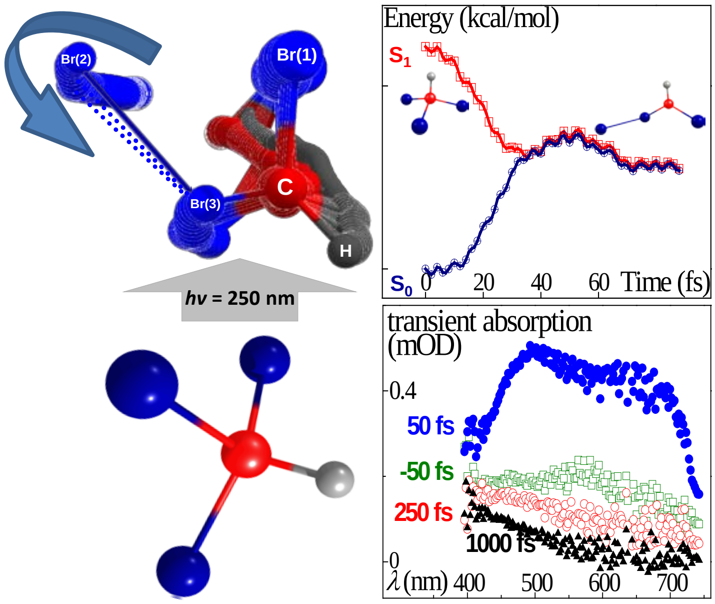


Figure 2. Gas-phase $CHBr_3$ upon 250 nm excitation into the lowest singlet excited S_1-state undergoes direct isomerization into the BrHCBr–Br species (top) identified through their 50-fs transient absorption between 450 and 700 nm (bottom). During isomerization, the partially dissociated bromine (Br(2), left) migrates to one of the two bromines of $CHBr_2$ while the carbon atom wanders between the bromine atoms of the $CHBr_2$ fragment in a 'roaming' motion.[12] The liquid-phase environment does not make any difference to the initial course of this isomerization as the formation of BrHCBr–Br occurs within 100 fs.

Further work[12] has demonstrated that following UV excitation of several geminal tribromides, including bromoform, what looks like simple fission of a carbon-bromine bond is in fact isomerization at fairly large distances via roaming of the molecular fragments, Fig. 2. This new and unusual roaming reaction path occurs not only in the gas phase, but also in solution. We carried out three experiments to unravel the roaming isomerization mechanism. First, solution-phase ultrafast transient absorption experiments showed the sub-100 fs isomerization of S_1 $CHBr_3$ into the BrHCBr–Br isomer species.

Similar isomerization is also observed for BBr_3 and PBr_3 in solution upon S_1 excitation. Second, similar to the solution phase, we observed that gas-phase S_1 $CHBr_3$ isomerises into BrHCBr–Br within 100 fs. Third, *ab initio* molecular dynamics simulations of XBr_3 (X = B, P, and CH) showed that photochemical reactivity in all three cases is governed by S_1/S_0 conical intersections, and can best be described as roaming-mediated pathways. As the excited-state potential flattens towards a S_1/S_0 conical intersection (~20 fs), the intramolecular forces give rise to large-amplitude wandering of the central atom (Z=CH, B, P) in the space between Br(1) and Br(3), Fig. 2. As the central Z-atom wanders, a nascent Br(2) fragment slowly roams away from the Br–Z–Br plane of a ZBr_2 fragment, with the partially dissociated Z–Br(2) bond through the intersection region. After the intersection, a barrierless reaction path continues on a gently-sloped region of the S_0 potential where Br(2) slips off the ZBr_2 bisector plane, pushes closer to one of the two bromines of the ZBr_2 fragment, and forms the Br–Br bond in the isomer product.

Bromoform is abundant in Nature. The practical consequence of roaming isomerization of this molecule is that it is thought to be followed by elimination of molecular bromine, leading to its increase in the atmosphere. Dissociation of molecular bromine is one of the key steps in ozone depletion chemistry, so establishing the photochemical connection between bromoform and bromine is important. Also of significance, roaming represents the deviation from the current chemical transformation paradigm, transition state theory, and needs to be taken into consideration in applications requiring knowledge of chemical reaction rates. This is especially important in the liquid phase, where about 70% of chemical transformations take place. We continue working on discovering, analyzing, quantifying of the unconventional photochemical dynamics in halogenated molecules. Our recent experiments demonstrate the occurrence of direct isomerization of S_1-excited CH_2I_2 in the gas-phase.[16] The UV laser pulse width used in the experiments (~30 fs), which is on a time scale of skeletal motion in halocarbons, allows direct-time resolution of this unusual dynamics and the population lifetimes of the isomer trapping site. The formation of the reactive isomeric species under atmospheric conditions influences the kinetics of the associated reactions by affecting the energy partitioning of the reaction products and may lead to unexpected reaction channels.

We acknowledge the NSF (CHE-0847707, CHE-0923360) and the Ohio Supercomputer Center (PCS0204) for support.

References.

1. Butler, L. J. *Annu. Rev. Phys. Chem.* **49**, 125-171 (1998).
2. Hertel, I. V.; Radloff, W. Rep. Prog. Phys. **69**, 1897-2003 (2006).
3. Bowman J. M.; Shepler, B. C. *Annu. Rev. Phys. Chem.* **62**, 531–553 (2011).
4. Townsend, D.; Lahankar, S. A.; Lee, S. K.; Chambreau, S. D.; Suits, A. G.; Zhang, X.; Rheinecker, J.; Harding, L. B.; Bowman, J. M. *Science* **306**, 1158-1161 (2004).
5. Phillips, D. L.; Fang, W.-H.; Zheng, X.; Wang, D.; Kwok, W. M. *Curr. Org. Chem.* **8**, 739-755 (2004).
6. Reid, S. A. *Int. Rev. Phys. Chem.* **33**, 341-370 (2014).
7. El-Khoury, P. Z.; Kwok, W. M.; Guan, X.; Ma, C.; Phillips, D. L.; Tarnovsky, A. N. *ChemPhysChem* **10**, 1895-1900 (2009).
8. El-Khoury, P. Z.; George, L.; Kalume, A.; Reid, S. A.; Ault, B. S.; Tarnovsky, A. N. *J. Chem. Phys.* **132***,* 124501 (2010).
9. El-Khoury, P. Z.; Pal, S. K.; Mereshchenko, A. S.; Tarnovsky, A. N. *Chem. Phys. Lett.* **493**, 61-66 (2010).
10. Pal, S. K.; Mereshchenko, A. S.; El-Khoury, P. Z.; Tarnovsky, A. N. *Chem. Phys. Lett.* **507**, 69-73 (2011).
11. Pal, S. K.; Mereshchenko, A. S.; Butaeva, E. V.; El-Khoury, P. Z.; Tarnovsky, A. N. *J. Chem. Phys.* **138**, 124501 (2013).
12. Mereshchenko, A. S.; Butaeva, E. V.; Borin, V. A.; Eyzips, A.; Tarnovsky, A. N. *Nat. Chem.* **7**, 562-568 (2015).
13. El-Khoury, P. Z.; Tarnovsky, A. N.; Schapiro, I.; Ryazantsev, M. N.; Olivucci, M. *J. Phys. Chem. A* **113**, 10767-10771 (2009).
14. El-Khoury, P. Z.; Tarnovsky, A. N. *Chem. Phys. Lett.* **453**, 160-166 (2008).
15. George, L.; Kalume, A.; El-Khoury, P. Z.; Tarnovsky, A.; Reid, S. A. *J. Chem. Phys.* **132**, 084503 (2010).
16. Borin, V. A.; Matveev, S. M.; Budkina, D. S.; El-Khoury, P. Z.; Tarnovsky, A. N. *Phys. Chem. Chem. Phys.* **18**, 128883-28892 (2016).

… OK, so what's the speed of dark?
(Steven Wright)

Light designs materials for light-conversion in photovoltaics

Federico Bella
GAME Lab, Department of Applied Science and Technology, Politecnico di Torino, Turin, Italy

A sustainable photovoltaics

Global energy supply system must be urgently reassessed exploiting the use of clean energy sources. To this purpose, investments for the development of renewable energy resources are increasing worldwide, with particular attention to the most mature technologies such as hydro, wind and solar power. In particular, photovoltaics stands out as the most effective technology to be intensively exploited, especially if one considers that the total solar energy absorbed by Earth in one hour is higher than the overall yearly energy use. Many different photovoltaic devices have been developed over the last sixty years, and the large-scale production of solar panels having good efficiencies has begun in the last decade and is rapidly growing. The major goal is to find a trade-off between efficiency, stability, cost and environmental impact of the solar cells. This has led to a lively scientific research in this direction, in a multidisciplinary environment that includes materials scientists, electronic engineers, technologists and experts of life cycle assessment.

The scientific community is currently working on two third-generation solar cells, i.e. the dye-sensitized solar cell (DSSC) and the perovskite solar cell (PSC).

The DSSC (Figure 1A) is a photoelectrochemical device proposed in 1991, composed of widely available and cheap materials [1,2]. Due to its ease of manufacture, versatility in the choice of components, good efficiency even in the presence of low irradiation level and adaptability to flexible substrates, DSSC has received considerable attention from the scientific community.

However, despite the record efficiency of 14.3% and the recent large-scale industrial production, DSSCs still suffer from poor long-term stability, mainly due to the presence of the volatile liquid electrolyte as well as photosensitive organic components.

The PSC (Figure 1B) emerged around 7 years ago, and it is based on a perovskite structured compound, most commonly a hybrid organic-inorganic lead, caesium or tin halide-based material as the light-harvesting active layer [3,4]. Sunlight conversion efficiencies of devices using these materials have increased from 3.8% in 2009 up to 22.1% in early 2016, thus making this the fastest-advancing solar technology to date. Besides this, perovskite materials are cheap to produce, simple to manufacture and upscalable also on building-integrated and flexible substrates.

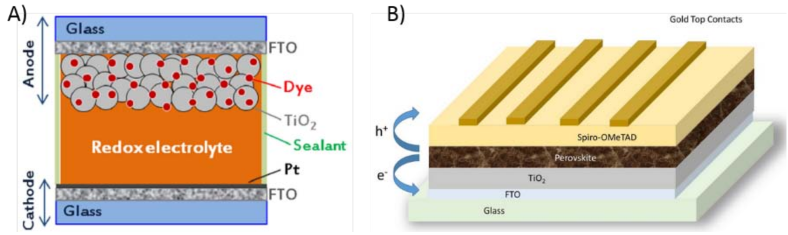


Figure 1. DSSC (A) and PSC (B) components. (Copyright: [5,6])

However, DSSCs and PSCs suffer of poor long-term stability. This is connected to the presence of liquid volatile components, hydrolytic phenomena induced by water permeation and UV-promoted photodegradation of some cell components. Multifunctional polymeric materials seem to be a viable solution in order to stabilized these third-generation solar cells. As regards the preparation of these advanced materials, photopolymerization can be considered as one of the most promising technique, due to its unique features such as rapidity and environmental friendliness, which are highly desired in a low impact and cheap technology like the PSC/DSSC ones.

Photopolymerization in 2016

Today, polymers are very popular in many different fields, and their use in nanotechnology and energy devices actively contributes to make them lighter and cheaper. However, the polymerization process itself must be considered when assessing costs and environmental impact of these technologies. For these reasons, the use of polymers in DSSCs and PSCs can be positively considered only if a cheap, low impact and quick polymerization technique is used, also guaranteeing excellent yields in terms of quality of the final products. The technique that exemplifies all of these aspects is photopolymerization, namely the polymerization (or crosslinking) process triggered by a visible or ultraviolet radiation [7]. This means that photochemistry plays a remarkable role also in the field of polymers, and light-induced polymerization represents its main application. Indeed, a large variety of polymeric materials can be obtained by means of *de novo* synthesis from low molar mass monomers, by polymerization (curing) of reactive mixtures comprising monomers or oligomers (pre-polymers) with different functionality, as well as by grafting processes (i.e., the synthesis of macromolecular branches from a single reactive unit). All these reactions can be effectively initiated by photoinitiators or/and photosensitizers.

Originally, UV-curing processes have been exclusively used in the field of coatings, inks and adhesives. In these fields, the peculiar features of this photoprocess are particularly advantageous: the polymer formation is a fast transformation (on the order of few minutes) of the liquid monomer into a solid film with tailored physico-chemical and mechanical properties; the process is solvent free, and usually carried out at ambient conditions. This brings about enormous advantages if compared with the long drying times of traditional paints, inks, varnishes, the environmental problems of the commonly used solvents-based processes and the great energy required for a thermal curing conducted in an oven. In the last decades, photopolymerization has been employed for several applications. In fact, the process can be carried out under a wide range of experimental conditions, including variations in monomer structures, number and type of reactive functional groups, irradiation rate, temperature, atmosphere and type of photoinitiator. Thus, the production of polymeric materials having tailor-made properties is possible. Light induced processes have also the special feature of guaranteeing spatial resolution, as the polymerization mainly occurs in the illuminated areas. In photolithography, light-induced insolubilization of photoresists is being used to produce the high definition images needed for manufacturing printing plates, optical disks and microcircuits. Today, UV-cured materials can be detected in mobile phones, displays, DVDs, telecommunications, domestic appliances, food and beverage containers, automotive, flooring, electronics, and many more. Photopolymerization is also involved in many intensively investigated technical platforms, such as microfluidic devices, energy storage electrolytes, nanocomposites for advanced applications, materials functionalization and surface modification. Moreover, most of the people have experienced a UV-curing process when their dental cavities were filled with materials preferably cured by a blue light. The photophysical and photochemical properties of all the materials obtained by light-induced polymerization have been extensively described in several review articles [8].

Photopolymerized components for DSSCs

The weakest component of a DSSC is the liquid electrolyte, where the redox shuttle (iodine- or cobalt-based) is dissolved in acetonitrile. Its volatility and flammability has limited the commercialization of stable solar panels. To fix this issue, photopolymerized electrolyte membranes (PEMs) have been proposed. Acrylate/methacrylate-based PEMs were prepared by UV curing, and then activated by swelling in an iodine/cobalt salt-based solution. Investigation of the mutual amounts of monofunctional and difunctional monomers, on the concentration of the redox mediator trapped in the polymeric network, and on the introduction of additives able to selectively enhance certain cell parameters led to efficiency values higher that 5% [9].

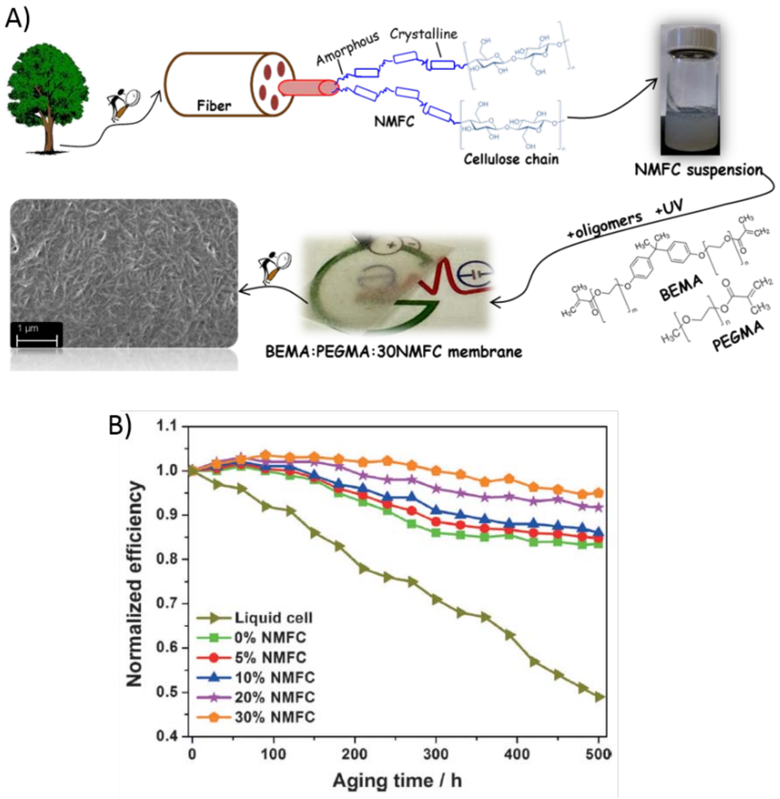


Figure 2. A) Preparation of a UV-cured PEM for DSSCs, additivated with NMFC; B) Aging test of the resulting DSSC. (Copyright: [10])

One of the advantages of the liquid-to-solid photopolymerization process lies in the possibility to introduce specific fillers. For example, the introduction and optimization of nanoscale microfibrillated cellulose (NMFC) in different amounts into photocured polymeric matrixes, resulting in bio-based, low-cost and highly efficient quasi-solid electrolytes for DSSCs, was reported (Figure 2A) [10]. All prepared biocomposite PEMs were characterized from the chemical, thermal, optical and mechanical point of view, and the beneficial effect of the amount of NMFC on the stability of the resulting material and the PV performance of the corresponding device was demonstrated. The positive effect of the NMFC filler was exerted on the photocurrent (by means of optical light-scattering phenomena) and on the photovoltage as well (through a shielding effect on the recombination phenomena). In the presence of the highest amount of filler (i.e., 30 wt%), efficiencies as high as 7.03 and 8.25% were achieved, at simulated light intensities of 1 and 0.4 sun, respectively. The NMFC positively affected also the long-term stability, as the same device demonstrated an excellent durability (i.e., > 95% efficiency retention after 500 h of extreme aging conditions, Figure 2B). Summarising, a novel smart filler able to cumulatively increase the photocurrent, the photovoltage and the long-term stability of a polymeric DSSC device was found and this was even more relevant if one considers that NMFC is a green biosourced material, and the composite polymer electrolytes were prepared through a rapid, solvent/catalyst-free process of photoinitiated polymerization. All the above demonstrated intriguing properties account for the remarkable potential prospects of the novel materials here proposed to be effectively implemented in the emerging business of polymeric DSSC manufacturing.

Photopolymerized components for PSCs

The stability of PSCs in humid environments, where also photochemical and thermal stresses are typically encountered, has presented an unsurmountable challenge to date. Photopolymers have been proposed in 2016 to fix two big issues of PSC, i.e UV- and H_2O-induced degradation of active components. In particular, a luminescent downshifting (LDS) fluoropolymeric layer was photogenerated on the front side of the device (i.e., glass-side), and it was able to prevent the UV portion of the incident solar spectrum to negatively interact with the PSC stack by converting it into visible light (also increasing cell efficiency) [11]. Photopolymers-based devices achieved efficiencies approaching 19% and, in order to increase atmospheric humidity tolerance, a strongly hydrophobic photopolymer was grown on the back contact side. The resulting PSCs demonstrated unrivalled stability in terms of PCEs during a 180-day aging test carried out under different atmospheric conditions and in the presence of various photochemical external stresses. Solar cells coated with the photopolymerized coating were also exposed to real outdoor conditions for more than 3 months, successfully demonstrating their exceptional tolerance to dust, soil and heavy rain on the external glass surface.

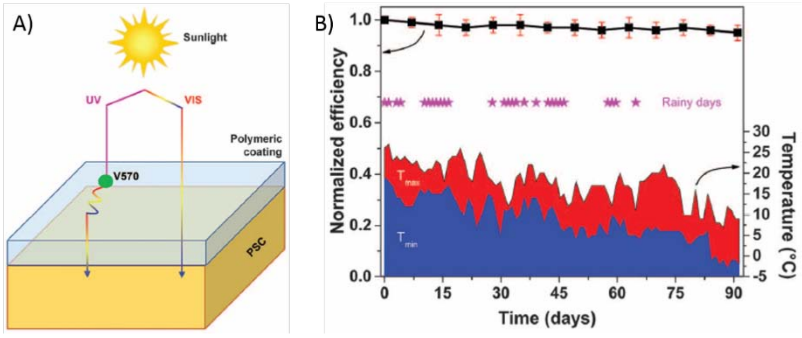


Figure 3. A) Operating principle of a LDS photopolymer; B) Aging test of the resulting PSC under outdoor conditions. (Copyright: [11])

References

[1] B. E. Hardin, H. J. Snaith, and M. D. McGehee, "The renaissance of dye-sensitized solar cells", *Nat. Photonics*, *6*, 162-169, **2012**. doi: 10.1038/nphoton.2012.22.

[2] M. Grätzel, "Dye-sensitized solar cells", *J. Photochem. Photobiol., C*, *4*, 145-153, **2003**. doi: 10.1016/S1389-5567(03)00026-1.

[3] H. J. Snaith, "Perovskites: The emergence of a new era for low-cost, high-efficiency solar cells", *J. Phys. Chem. Lett.*, *4*, 3623-3630, **2013**. doi: 10.1021/jz4020162.

[4] P. Gao, M. Grätzel, and M. K. Nazeeruddin, "Organohalide lead perovskites for photovoltaic applications", *Energy Environ. Sci.*, *7*, 2448-2463, **2014**. doi: 10.1039/c4ee00942h.

[5] F. Bella, "Polymer electrolytes and perovskites: Lights and shadows in photovoltaic devices", *Electrochim. Acta*, *175*, 151-161, **2015**. doi: 10.1016/j.electacta.2015.02.195.

[6] "Constructing a perovskite solar cell", https://www.youtube.com/watch?v=crAugJXG3QA, accessed November 2016.

[7] E. Andrzejewska, "Photopolymerization kinetics of multifunctional monomers", *Prog. Polym. Sci.*, *26*, 605-665, **2001**. doi: 10.1016/S0079-6700(01)00004-1.

[8] J. V. Crivello, and E. Reichmanis, "Photopolymer materials and processes for advanced technologies". *Chem. Mater.*, *26*, 533-548, **2014**. doi: 10.1021/cm402262g.

[9] F. Bella, D. Pugliese, J. R. Nair, A. Sacco, S. Bianco, C. Gerbaldi, C. Barolo, and R. Bongiovanni, "A UV-crosslinked polymer electrolyte membrane for quasi-solid dye-sensitized solar cells with excellent efficiency and durability", *Phys. Chem. Chem. Phys.*, *15*, 3706-3711, **2013**. doi: 10.1039/c3cp00059a.

[10] A. Chiappone, F. Bella, J. R. Nair, G. Meligrana, R. Bongiovanni, and C. Gerbaldi, "Structure-Performance Correlation of Nanocellulose-Based Polymer Electrolytes for Efficient Quasi-solid DSSCs", *ChemElectroChem*, *1*, 1350-1358, **2014**. doi: 10.1002/celc.201402051.

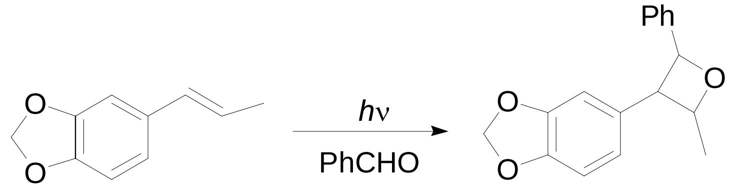
[11] F. Bella, G. Griffini, J. P. Correa-Baena, G. Saracco, M. Grätzel, A. Hagfeldt, S. Turri, and C. Gerbaldi, "Improving efficiency and stability of perovskite solar cells with photocurable fluoropolymers", *Science*, *354*, 203-206, **2016**. doi: 10.1126/science.aah4046.

PILLS OF HISTORY

An article of Ciamician on the reaction between a carbonyl compound and an alkene in the same year of the article of Paternò

Maurizio D'Auria
Dipartimento di Scienze, Università della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

Here we reported some pages of the article published by Ciamician and Silber on *Berichte der deutschen chemischer Gesellshaft* **1909**, *42*, 1386-1391. In this article, between other reactions, the reaction between safrol and isosafrol with benzaldehyde has been described (Scheme 1). The authors showed that the reaction product was an adduct.



Scheme 1

The authors did not propose the stucture oft he adduct, but now we know that probably it was the corresponding oxetane. It is interesting to note that this article was published in the same year of the article of Paternò and Chieffi where the oxetane structure was proposed (E. Paternò and G. Chieffi, *Gazz. Chim. Ital.* **1909**, *39*(I), 341-361).

Benzaldehyd und Safrol und Isosafrol

Aus den interessanten Versuchen von Benrath1), die eine Fortsetzung der bekannten Klingerschen Versuche bilden, weiß man, daß das Benzaldehyd unter dem Einfluß des Lichts sich an viele Körper addiert, um so vershiedene Kondensationsprodukte zu bilden. Wir haben nun, gleichzeitig mit den erwähnten Versuchen, sehen wollen, ob sich Safrol und Isosafrol Benzaldehyd gegenüber verschieden verhalten. In diesem Fall reagieren nun beide Isomere und liefern Additionsprodukte von derselben Formel “$C_7H_6O.C_{10}H_{10}O_2$”; hiermit ist aber noch nicht gesagt, daß die beiden Isomeren ein analoges Verhalten haben, denn die Konstitution der beiden Produkte kann, je nachdem die Reaktion stattfindet, verschieden sein. Während eines Jahres haben wir gleichzeitig 16 g Safrol und 16 g Isosafrol, gemischt je mit 10 g Benzaldehyd, belichtet. Die entstandenen harzigen Produkte wurden zunächst von den unangegriffen gebliebenen Körpen mittels einer Destillation mit Wasserdampf getrennt. As 16 g Safrol und Isosafrol erhielten wir 21 g bezw. 18 g Harzrückstand.

Der vom Safrol herstammende wurde wiederholt mit Alkohol ausgekocht; das zurückbleibende, in Alkohol sehr schwer lösliche Harzpulver schmolz zwischen 150-180°, und gab bei der Analyse Zahlen, die für die oben angedeutete Zusammensetzung sprechen:

$(C_7H_6O + C_{10}H_{10}O_2 =)\ C_{17}H_{16}O_3$. Ber. C 76.12, H 5.97.
Gef. » 75.63, » 6.07.

Der aus dem Isosafrol gebildete Harzrückstand unterlag einer gleichen Behandlung mit Methylalkohol. Beim wiederholten Behandeln in der Kälte blieb schließlich ein weißes, amorphes, zwischen 170-180° schmelzendes Pulver zurück, das bei der Analyse die gleichen Zahlen wie oben gab.

$C_{17}H_{16}O_3$. Ber. C 76.12, H 5.97.
Gef. » 75.63, » 6.07.

EPA IS ON FACEBOOK

European Photochemistry Association
44 "Mi piace" · 4 ne parlano

Organizzazione
European Photochemistry Association

Invita i tuoi amici a cliccare su "Mi piace" su questa Pagina

European Photochemistry Association ha condiviso un link.
1 febbraio

ıbe Optics and Nanospectroscopy
Germany

Home
www.wonton2015.org

The WONTON conference series focusses on advancing the understanding of photophysical properties and the spectroscopy of nanoscale system with emphasis on carbon nanotubes and other nanocarbon materials.

European Photochemistry Association ha condiviso un link.
1 febbraio

Canadian Light Source / Centre Canadien de rayonnement synchrotron
www.lightsource.ca

The Canadian Light Source is committed to being a world-leading centre of excellence in synchrotron science and its applications by working with the scientific community to promote the use of synchrotron light, promoting...

European Photochemistry Association ha condiviso un link.
1 febbraio

European Photochemistry Association ha condiviso un link.
1 febbraio

NEWS: Congress announcement:
First announcement of the 2015 International Workshop on Nanotube Optics and Nanospectroscopy (WONTON '15).
The workshop will take place from
1 - 4, June 2015
at Banz Abbey, a former Benedictine Monastery in upper Franconia, Germany.

Additional information on the workshop will be posted at www.wonton2015.org.

ıbe Optics and Nanospectroscopy
Germany

Home
www.wonton2015.org

The WONTON conference series focusses on advancing the understanding of photophysical properties and the spectroscopy of

https://www.facebook.com/pages/European-Photochemistry-Association/568823339798749?fref=ts

join EPA on Facebook ....

Masuhara Lectureship Award

Hiroshi Masuhara received MUKAI PRIZE from Tokyo Ohka Foundation for the Promotion of Science and Technology on June 1, 2010 for his scientific achievement on "Molecular Photo-Science Explored by Lasers". He donated this auxiliary money to Asian and Oceanian Photochemistry Association (APA) to assist its further development. At that time Executive members and councilors asked some corporate members to contribute for supporting Asian and Oceanian Photochemistry Conference (APC) and started Masuhara Lectureship Award. This is set in honor of Hiroshi Masuhara who is the funding president (2002-2004) of APA.

Initially one awardee and then two awardees have been selected by voting in the corresponding committee. Now one is from Asian and Oceanian photo-scientist and the other is from outside Asia, The past awardees are as follows.

2012 APC at Osaka, Johan Hofkens (KULeuven)

2014 APC at Trivandrum, Thomas Ebbesen (Strasbourg) and Yoshihisa Inoue (Osaka)

2016 APC at Singapore, Gregory Scholes (Princeton) and Vivian V. V. Yam (Hong Kong).

Summarized by Hiroshi Masuhara, December 11, 2016.

For information on the Asian and Oceanian Photochemistry Association, see http://www.asianphotochem.com/index.html.

CONFERENCE REPORTS

4x1=5. The first Joint Congress of French and Italian Photochemists and Photobiologists

Monday morning, September 19th. Something very basic has probably been forgotten. Undoubtedly! Nevertheless, no time to spear: the first vanguards of congress attendees are climbing up the stairs of the Student Centre of the Università degli Studi in Bari, Italy. As the first participant registers, the first Joint Congress of the French and Italian Photochemists and Photobiologists moves into reality. Photochemistry and Photobiology are scientifically related and share a common ground: Photochemical and Photobiological Sciences, the publication jointly owned by the European Society of Photobiology and the European Photochemical Society, is a proof of the contiguity of these two research areas. Unfortunately, no joint conference was yet organized and this lack of interaction on the personal ground is often an obstacle to cross-contamination between the two cousin disciplines. Indeed the purpose of congresses and conferences is not to allow researchers good sightseeing and show off themselves. They are the ideal place to listen and become curious, to criticize and discuss issues, to talk and to share ideas and, eventually, to spur collaborations.

This year the *Groupe français de photochimie, photophysique et photosciences* (**GFP2P**), the *Gruppo Italiano di Fotochimica* (**GIF**), the *Société Française de Photobiologie* (**SFPb**) and the *Società Italiana di Fotobiologia* (**SIFB**) have joined efforts and organised the first Joint Congress of the French and Italian Photochemists and Photobiologists: **160** researchers from the two countries presenting their most recent scientific results. Few figures will help in describing the congress: **2** plenary lectures, **13** keynote lectures, and **74** oral communications were delivered in 6 joint and 10 parallel sessions. More than **30** poster contributions were also present. Great attention was given to PhD students, post-docs, and early stage researchers who delivered **3** keynote lectures (Raffaello Mazzaro GIF PhD Prize awardee, Filippo Monti and Davide Ravelli winners of the GIF Young Investigator Award) and **39** oral communications. Financial support from the societies allowed funding **40** fellowships to Italian and French PhD students and post-docs.

Jacques Piette, from GIGA-Research – Université de Liège, delivered a lecture entitled *RIP3 antagonizes a TSC 2-mediated pro-survival pathway in Photodynamic therapy-induced glioblastoma cell death*. Jacques presented the investigation ongoing in his laboratory on the pathways involved in cell death and the survival mechanisms occurring in glioblastoma following 5-aminolevulinic acid (5-ALA)-based photodynamical therapy of human glioblastoma cells (LN-18).

Luisa De Cola's lecture entitled *Seeing, understanding and controlling self-assembly of luminescent species* illustrated the use of Platinum complexes as building block for luminescent reversible piezochromic and mechanochromic materials. She showed the researches performed at the Institut de Science et d'Ingénierie Supramoléculaires in Strasburg focused on how to control the assemblies and obtain uniform size of the aggregate that can even be converted in thermodynamic unstable species by light.

The next joint conference? Too early to say when and where it will be organized, but this one that was wrapped out in September is the proof-of-concept that summing up four (societies) turns out to five.

Massimo Trotta

Porter's Medal 2016 Ceremony

Professor James Barber FRS of Imperial College London and one to Professor Fredrick Lewis of Northwestern University, received the Porter's Medal at the 9th Asian Photochemistry Conference (APC2016) held at the Nanyang Technological University (NTU), Singapore from the 4th to 8th December, 2016. As the President of the EPA, Prof Pérez-Prieto introduced Prof James Barber, while Prof Malcolm Forbes, Past President of the Inter-American Photochemistry Association, introduced Prof Frederic Lewis. James Barber presented the lecture entitled "Photosynthesis: The Photochemical Process That Powers Our Planet" and Frederick Lewis presented the lecture "The Mechanism of DNA Charge Transport. A Twenty-year Search".

James Barber's Lecture

Fred Luis's Lecture

Prof James Barber's Lecture

Prof Barber focused on his work to elucidate the photochemistry of water splitting which is the most fundamental energy converting reaction of photosynthesis. It is this reaction which has generated, and maintains the oxygen in the atmosphere, as well as providing the reducing equivalents to power the reduction of CO2 and create the organic molecules of life and, therefore, of fossil fuels. Barber described how his research over many years played a leading role in unravelling the details of the photosynthetic water splitting reaction which occurs in a large multi-protein complex binding chlorophyll and carotene molecules known as Photosystem II (PSII). Using X-ray diffraction analyses of crystals of this complex, he and his colleagues at Imperial College, revealed the catalytic center to be a Mn3CaO4 cubane with the fourth Mn attached to cubane by one of its oxo bridging bonds. This organization of the metal ions and the properties of the protein cavity in which they are contained, suggests a mechanism for the O-O bond formation. As emphasized by Barber in his lecture, it seems highly likely that water splitting involves oxidation chemistry occurring on the Mn ion outside the cubane which is adjacent to the Ca2+. Here a highly electrophilic oxo or oxyl radical is probably formed at the final stage of the four electron extraction catalytic cycle which would then be poised for nucleophilic attack from the oxygen of the second substrate water located within the coordination sphere of the Ca2+. As he explained his finding has provided a "blue print" for developments in artificial photosynthesis, an area of research which Professor Porter initiated over 40 years ago. Through a Visiting Professorship to NTU, he has established the Solar Fuels Laboratory within the School of Material Sciences. In this way he is collaborating with chemists, electrochemists and material scientists to develop exciting photochemical and electrochemical catalysts which split water making hydrogen available as an energy source. In particular he described his recent achievements with nano-structured hematite as a photoanode to generate oxygen from water.

I am very grateful to Prof James Barber for helping in summarizing his lecture.

Julia Pérez Prieto

5th HRSMC Summer School Photochemistry 2016 - Fundamentals, and Applications, August 27-31, Hotel Vaeshartelt, Maastricht, The Netherlands

At the end of august 2016, the sunniest month ever remembered in The Netherlands, the 5th HRSMC Summer School in Photochemistry took place in Maastricht, 4 years after the last edition in Wijk aan Zee. The event was located at the Hotel Buitenplaats Vaeshartelt, a magnificent palace in South Limburg adapted as a hotel for conventions. In this edition the organizing committee was composed by Fred Brouwer (UvA), Sylvestre Bonnet (UL), and Gert van der Zwan (VU), with the help of Ineke Weijer and Hilde Zwaan-van der Plas (HRMSC). More than 40 PhD students from all over Europe joined to learn more about the different fields in photochemistry in a five days school consisting of lectures, poster sessions, and a social event.

The first day, before the official program started, the students received an introductory talk by Sylvester Bonnet, where all the basic concepts in the field were refreshed in a very entertaining quiz format. After Dr. Bonnet's talk, Prof. Brouwer took the stage to introduce a riddle to think about during the following days: which white powdery substance, available at any supermarket, quenched the blue fluorescence emitted from a glass containing a water-like liquid when illuminated by a UV lamp, and by what mechanism?

During the event two poster sessions were scheduled on Monday and Tuesday after dinner, which allowed the participants to share their research with their colleagues, getting interesting feedback and new ideas in a very relaxed atmosphere (with the help of some drinks and snacks). Besides the traditional poster session, the main lectures occupied most of the time. There were six international invited lecturers, having each of them three slots of 45 minutes spread over three different days. This format allowed the students to have time to process all the new information and, also very important, to interact with the lecturers, since they were involved in the same activities for, at least, three full days. Furthermore, at the end of each session, the participants were divided in groups of approximately 10 students in which they discussed about the different topics of the lectures. Clever questions for the lecturers arose from those worthwhile discussions.

Sometimes these scientific (or non-scientific) discussions even crossed the classroom and became conversation topics during the meals or in the bar. A brief summary of the lectures is given bellow:

Gary W. Brudvig (New Haven, U.S.A.) took it upon himself to guide us through how nature works focusing on solar energy conversion, so it can be used to improve the use of sunlight as energy source.

Paola Ceroni (Bologna, Italy) familiarized us with the world of light-harvesting antennae, by explaining us the topic from the basics to apply it. Two great examples were shown where the efficiency of the antennae process got up to really high values.

Phoebe Glazer (Kentucky, U.S.A.) very nicely explained us how photochemistry can help on the treatment of some diseases such as cancer. The photodynamic therapy (PDT) and photoactivated chemotherapy (PACT) have great advantages, especially on the patient, due to its lower damaging effects.

Stefan Hecht (Berlin, Germany) had the challenging task of showing us the wide range of applications that photochemistry has nowadays. He focussed on three main processes where this topic can be used: photoinduced scission, stitching and switching.

Massimo Olivucci (Siena, Italy / Bowling Green, USA) had the challenging pleasure of teaching us the essential computational photochemistry concepts in order to understand and apply it in our lives.

Claus Seidel (Düsseldorf, Germany) illustrated us with the interesting world of fluorescence. Furthermore, he showed us how we could obtain different types of information from a single experiment.

In addition to that, other special lectures were given. The first one was about optical lithography by Roel Gronheid, where we learnt the basic concepts of information storage using chemistry and different types of light (from visible to extreme UV). The second one, by Axel Wiegand, deepened into detectors. We learnt how to choose the best type of detector depending on the empirical conditions and the type of experiment performed. Moreover, four brave students had the chance to expose their work in front of the audience. There we learnt from molecular switches to contacts and frictions of surfaces, and fluorescence, which can be applied as theranostics agents for therapy.

During the second day we spent the afternoon on a very enjoyable social event. Its nature was kept completely as a secret, the only clue given to us was that we should wear very comfortable cloths. We were all very much surprised when we arrived to the famous caves of

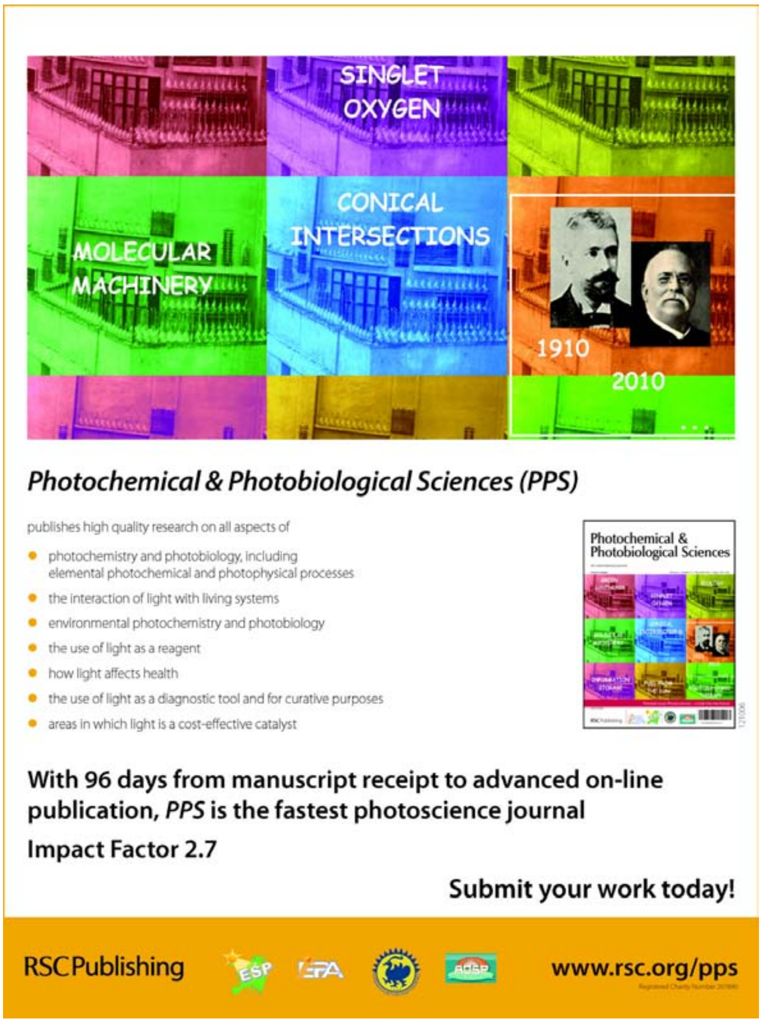
Maastricht. Inside a laser tag match was waiting for us. We were divided into different groups and we fought against the others in the incredible environment that the underground of Maastricht provided us. After relaxing with a drink we climbed to the top of a hill from where we took a car each and drove it to the bottom of the hill, enjoying the speed that you can get. After going up and down several times, we went to what apparently was going to be a normal visit to another cave. We got again surprised by discovering the amazing and scary story that the place had. It was a fantastic and very well organized event where everybody could enjoy, meet, and talk to other people. The event finished with a very tasty dinner with very nice views.

To sum up, the five days of this summer photochemistry school were extremely fruitful both personally and scientifically speaking. In one hand, we have learnt large amounts of new photochemical concepts that for sure will be very useful to improve our PhD thesis. On the other hand, we have also made a lot of new friends from north, south, inland, and across the seas. Finally, we extremely encourage the next generation of photochemistry PhD students to assist to the next summer school.

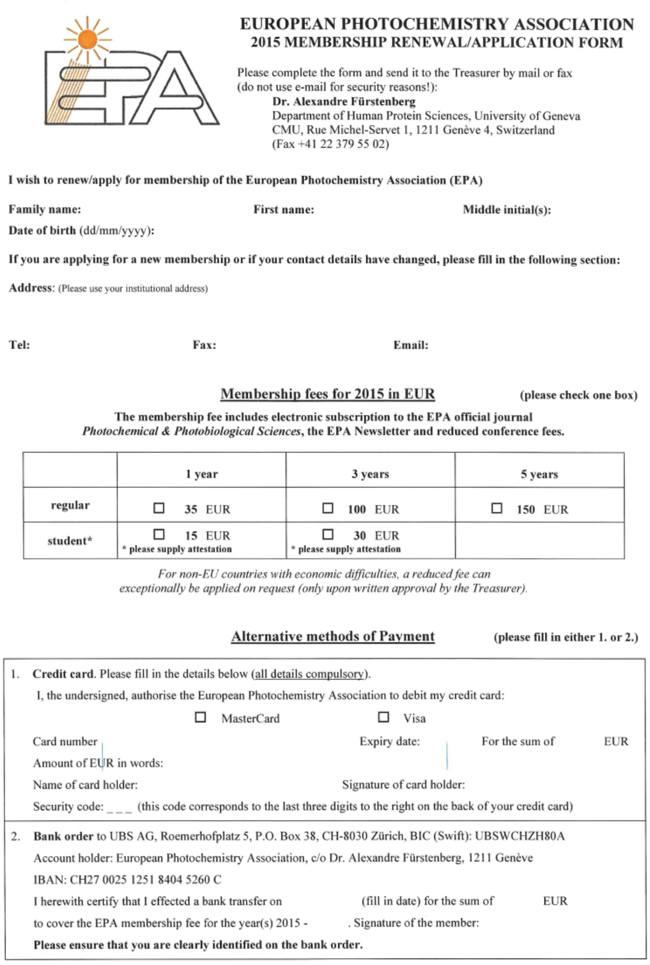
On behalf of all participants,

Jordi-Amat Cuello-Garibo (UL), Elena Caballero (Universidad de Castilla-La Mancha), & Roger Bresolí (Universitat Ramon Llull)

PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



MEMBERSHIP APPLICATION FORM



EUROPEAN PHOTOCHEMISTRY ASSOCIATION
2015 MEMBERSHIP RENEWAL/APPLICATION FORM

Please complete the form and send it to the Treasurer by mail or fax
(do not use e-mail for security reasons!):
Dr. Alexandre Fürstenberg
Department of Human Protein Sciences, University of Geneva
CMU, Rue Michel-Servet 1, 1211 Genève 4, Switzerland
(Fax +41 22 379 55 02)

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

Family name: **First name:** **Middle initial(s):**
Date of birth (dd/mm/yyyy):

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

Address: (Please use your institutional address)

Tel: **Fax:** **Email:**

Membership fees for 2015 in EUR **(please check one box)**

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

	1 year	**3 years**	**5 years**
regular	☐ **35** EUR	☐ **100** EUR	☐ **150** EUR
student*	☐ **15** EUR *** please supply attestation**	☐ **30** EUR *** please supply attestation**	

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

Alternative methods of Payment **(please fill in either 1. or 2.)**

1. **Credit card**. Please fill in the details below (all details compulsory).
   I, the undersigned, authorise the European Photochemistry Association to debit my credit card:
   ☐ MasterCard ☐ Visa
   Card number Expiry date: For the sum of EUR
   Amount of EUR in words:
   Name of card holder: Signature of card holder:
   Security code: _ _ _ (this code corresponds to the last three digits to the right on the back of your credit card)
2. **Bank order** to UBS AG, Roemerhofplatz 5, P.O. Box 38, CH-8030 Zürich, BIC (Swift): UBSWCHZH80A
   Account holder: European Photochemistry Association, c/o Dr. Alexandre Fürstenberg, 1211 Genève
   IBAN: CH27 0025 1251 8404 5260 C
   I herewith certify that I effected a bank transfer on (fill in date) for the sum of EUR
   to cover the EPA membership fee for the year(s) 2015 - . Signature of the member:
   Please ensure that you are clearly identified on the bank order.